RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

by

JAMES A. KNIGHT

and

COLEMAN J. BRYAN

Project No. A-446-8

United States Atomic Energy Commission

Division of Isotopes Development

Contract No. AT (38-1)-202

Engineering Experiment Station
Georgia Institute of Technology
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Final Report.

Knight, James A., Jr.
May 1, 1960--February 28, 1963

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
May 31, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 1, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from May 1 to May 31, 1960

Gentlemen:

The broad objectives of this project, initiated on May 1, 1960, are to study the effects of ionizing radiation on the cyanogenation of organic compounds. The organic compounds to be studied are specific representatives of the alkanes, alkenes and aromatic hydrocarbons. Chemical reagents that can be used for cyanogenation are: (a) cyanogen, $(CN)_2$; (b) the cyanogen halides; and (c) hydrogen cyanide, HCN. Initial attention will be given to the system of benzene and cyanogen. The cesium-137 irradiator will be utilized in this program.

A search of the literature on radiation-induced cyanogenation of organic compounds revealed only one reference to this subject. In the February 5, 1960, issue of the J. Am. Chem. Soc., McKusick, et al., reported on the cyanogenation, effected by 2-mev electrons, of benzene, toluene, and cyclohexane with hydrogen cyanide.

Mr. Coleman Bryan, a graduate student in the School of Chemistry, has been employed and will start to work on the project on a full-time basis June 1. He has completed most of the requirements for the M. S. degree and will complete the remaining requirements during the coming academic year. Dr. James A. Knight, Jr., project director, will devote one-fourth time to the project.

During the coming month, attention will be given: (a) to the preparation, purification and handling of cyanogen; (b) to the design of irradiation experiments so that hazards will be reduced to a minimum; and (c) to the design and fabrication of a vacuum system for the sampling of gaseous radiolysis products. The procurement of necessary equipment for the program will be initiated.

The laboratory work for this program will be carried out mainly in the Radioisotopes Laboratory, which also houses the cesium-137 source.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

June 30, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 2, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from June 1 to June 30, 1960

Gentlemen:

Due to the extreme toxicity of cyanogen, careful attention has been given to the procedures and apparatus to be used in the preparation and handling of cyanogen so that hazards will be reduced to a minimum. The method to be used for the preparation of cyanogen is given in Inorganic Syntheses, Vol. 5, and the necessary chemicals and equipment have been obtained. All preparations and transfer work will be carried out in a well-ventilated hood.

Reaction tubes and a holder for the reaction tubes have been designed and fabricated. The brass sample holder has been designed so that it can be evacuated constantly during an irradiation involving a cyanating agent, and provision will be made to monitor the temperature during an irradiation. A gas-sampling system for the sampling of gaseous radiolysis products has been designed and fabricated.

Dosimetry studies were made with the ferrous ion dosimeter in outside sample tube No. 12 of the cesium-137 irradiator and the dose was found to be 7.58×10^5 rad/hr.

Methods for the preparation of cyanogen halides were checked and several selected as possibilities for future work.

During the coming month, attention will be given: (a) to the preparation of cyanogen; (b) to determination of the solubility of cyanogen in benzene; and (c) to preliminary irradiations of the benzene-cyanogen system.

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

Respectfully submitted,

James A. Knight, Jr.
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
August 31, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 3, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from August 1 to August 31, 1960

Gentlemen:

During the past month, six irradiations have been made in the Cesium-137 Research Irradiator. Four of these irradiations were cyanogen-benzene mixtures: one, pure benzene; and one, pure cyanogen.

After an irradiation of a cyanogen-benzene mixture, the remaining cyanogen was determined by extraction of the cyanogen with potassium hydroxide solution followed by titration with standard silver nitrate solution. The benzene phase, after drying over anhydrous magnesium sulfate, was distilled. The portion boiling up to 78.5° C was collected as distillate. Infrared spectra on both the distillate and flask residue were obtained and compared with reference spectra. Infrared spectra for reference and comparison were obtained on: (a) pure benzene, (b) a 3-per-cent solution of benzonitrile in benzene, (c) a 10-per-cent solution of benzonitrile in benzene, (d) irradiated benzene, and (e) flask residue from distillation of irradiated benzene.

The results of the irradiations of the cyanogen-benzene mixtures are given in Tables I and II.

TABLE I

IRRADIATIONS OF CYANOGEN-BENZENE MIXTURES

Irradiation No.	Irradiation Mixtures: Cyanogen (Moles)	Irradiation Mixtures: Benzene (Moles)	Period of Irradiation (Hours)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
1	0.0052	0.11	3	0.0022	0.0030	1.6×10^{20}
3	0.0097	0.11	8	0.0041	0.0056	4.2×10^{20}
4	0.0102	0.11	7	0.0052	0.0050	3.6×10^{20}
6	0.0174	0.275	18	---[a]	---	9.5×10^{20}

[a] It was not possible to titrate this sample due to the black color of the potassium hydroxide phase.

TABLE II

COMMENTS ON INFRARED SPECTRA

Irradiation No.	Distillate	Residue in Flask
1	Very similar to pure benzene	Identical with flask residue of irradiated benzene
3	Very similar to pure benzene	Identical with flask residue of irradiated benzene
4	Very similar to pure benzene	Identical with flask residue of irradiated benzene
6	Identical to pure benzene	Identical with flask residue of irradiated benzene

Pure cyanogen, 0.0246 mole, was irradiated for 5 hours. The cyanogen remaining after irradiation was determined as mentioned above and found to be 0.0198 mole, indicating that 0.0048 mole of cyanogen had polymerized. This quantity is fairly close to the quantities of cyanogen consumed in irradiations 3 and 4 of the cyanogen-benzene mixtures.

During the coming month, attention will be given: (a) to consideration

of a stainless steel irradiation vessel in order that irradiations can be performed on mixtures under higher pressure, (b) to the determination of the solubility of cyanogen in toluene and cyclohexane, and (c) to irradiations of the cyanogen-toluene system and of the cyanogen-cyclohexane system.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

September 30, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 4, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from September 1 to September 30, 1960.

Gentlemen:

During the past month, three irradiations have been made in the Cesium-137 Research Irradiator: (1) cyanogen-toluene mixture, (2) cyanogen-n-heptane, and (3) cyanogen-benzene. Additional solubility studies were also conducted in which the solubilities of cyanogen in benzene, cyclohexane, toluene, n-heptane, 2,4,4-trimethylpentene-1, and 2,2,4-trimethylpentane at 25.0° C were determined.

The irradiated mixtures were treated as follows: After irradiation, the remaining cyanogen was determined by extraction with potassium hydroxide followed by titration with a standard silver nitrate solution. The organic phase, after drying over magnesium sulfate, was distilled. Infrared spectra on both the distillates and flask residues were obtained and compared with reference spectra. The results of the three irradiations are summarized in Tables I and II.

TABLE I

IRRADIATIONS OF CYANOGEN-ORGANIC MIXTURES

Irradiation Mixture No.	Organic Compound (Moles)	Cyanogen (Moles)	Period of Irradiation (Hours)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
7	Toluene, 0.246	0.0352	24	0.0067	0.0285	1.27×10^{21}
8	n-Heptane, 0.171	0.0308	72	0.01152	0.0193	3.81×10^{21}
9	Benzene, 0.275	0.0242	163	0.0202	0.0040	8.62×10^{21}

TABLE II

COMMENTS ON INFRARED SPECTRA

Irradiation No.	Distillate	Residue in Flask
7	Very similar to pure toluene	No nitrile peak observed
8	Identical to pure n-heptane	Possible nitrile peak observed at 4.4 microns
9	Complete results have not been obtained for this irradiation.	

The adsorption peak at 4.4 microns from the infrared spectra from the residue of the irradiated cyanogen-n-heptane mixture indicates very strongly that cyanogenation occurred. Additional irradiations of this mixture will be made so that a more thorough and complete analysis of the irradiated mixture can be made.

The solubility studies were made in a tube fitted with a ground glass cap to which a stopcock and a U-manometer were attached. The tube was first cooled in a dry ice-acetone bath and the organic liquid and cyanogen added. After partial equilibration at 5° C, the tube and contents were equilibrated in a constant temperature bath at 25.0° C. The cyanogen was then extracted with potassium hydroxide and titrated with a standard silver nitrate solution. The results are summarized in Table III.

TABLE III

SOLUBILITY OF CYANOGEN IN ORGANIC LIQUIDS AT 25.0° C

Compound	Mole Cyanogen/10 ml Organic	ml Cyanogen/ml Organic
Benzene	0.0144	32.2 ± 0.6
Toluene	0.0156	35.0 ± 0.2
Cyclohexane	0.0079	17.7 ± 0.2
n-Heptane	0.0091	20.4 ± 0.2
2,4,4-Trimethylpentene-1	0.0105	23.5 ± 0.1
2,4,4-Trimethylpentane	0.0091	20.4 ± 0.4

During the coming month, attention will be given to: (a) fabrication of additional reaction tube holders, (b) dosimetry studies in additional holes in the cesium-137 source, and (c) irradiations of cyanogen-2,2,4-trimethylpentane, cyanogen-cyclohexane, and cyanogen-n-heptane mixtures.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
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Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
November 30, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 5, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from November 1 to November 30, 1960

Gentlemen:

During the past month, five irradiations have been made in the Cesium-137 Research Irradiator: (1) cyanogen-2,4,4-trimethylpentene-1, (2) cyanogen-2-methylpentane, (3) cyanogen-3-methylhexane, (4) pure 2-methylpentane, and (5) pure 3-methylhexane. The stainless steel bomb which will be used as an irradiation tube has been obtained. The gas chromatographic unit has been received and is being placed in operation. Two blank experiments of mixtures of cyanogen-organic compounds were carried out in the same manner as the irradiation experiments except for exposing the mixture to the high energy radiation.

The irradiated mixtures were treated in the usual manner, and the results are summarized in Tables I and II. The irradiated pure organic compounds, 2-methylpentane and 3-methylhexane, were distilled, and infrared spectra were obtained on the distillate and residue of each for reference purposes.

TABLE I

IRRADIATIONS OF CYANOGEN-ORGANIC MIXTURES

Irradiation Mixture No.	Organic Compound (Moles)	Cyanogen (Moles)	Period of Irradiation (Hours)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
19	2,4,4-Trimethylpentene-1(0.150)	0.0306	168	0.0227	0.0079	8.89×10^{21}
21	2-Methylpentane(0.206)	0.0220	168	0.0127	0.0093	8.89×10^{21}
22	3-Methylhexane(0.172)	0.0298	168	0.0200	0.0098	7.65×10^{21}

TABLE II

COMMENTS ON INFRARED SPECTRA

Irradiation No.	Distillate	Residue in Flask
19	Very similar to pure 2,4,4-trimethylpentene-1	Possible nitrile peak at 4.4 microns and possible amine peak at 2.9 microns
21	Identical to pure 2-methylpentane	Possible nitrile peak at 4.4 microns and possible amine peak at 3.0 microns
22	Identical to pure 3-methylhexane	Possible nitrile peak at 4.4 microns and possible amine peak at 2.98 microns

Two blank experiments of mixtures of cyanogen with 2,4,4-trimethylpentene-1 and n-heptane were carried out to establish if any reaction occurred in the absence of high energy irradiation. The mixtures were sealed in glass irradiation tubes. After standing at room temperature (23°C) for 168 hours, the mixtures were treated the same as an irradiated mixture. The cyanogen remaining indicates that no reaction took place in either case. Gas chromatographic analysis of the organic phase from each experiment showed only the pure compound was present. Infrared curves of the organic phase did not show any absorption that could be attributed to the cyano group. The results of the two blank experiments show that no reaction of cyanogen with the organic compounds occurred. The results are summarized in Table III.

TABLE III

BLANK EXPERIMENTS OF CYANOGEN-ORGANIC MIXTURES

Blank Experiment No.	Organic Compound (Moles)	Cyanogen (Moles)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)
1	2,4,4-Trimethylpentene-1 (0.160)	0.0226	0.0225	0.0001
2	n-Heptane (0.171)	0.0280	0.0276	0.0004

During the coming month, attention will be given to: (a) irradiations in a stainless steel reaction bomb so that higher molar ratios of cyanogen to hydrocarbon can be employed, (b) dosimetry studies of the center hole of the Cesium-137 Irradiator, and (c) further characterization of the products from the irradiated mixtures.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

December 31, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 6, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from December 1 to December 31, 1960

Gentlemen:

During the past month, two irradiations have been made in the Cesium-137 Research Irradiator: (1) cyanogen-cyclohexane in a glass irradiation tube, and (2) cyanogen-benzene in a stainless steel bomb. Further calibration work has been done with the gas chromatographic unit. Dosimetry studies have been completed on the center hole with the stainless steel bomb containers.

The cyanogen-cyclohexane irradiation was treated in the usual manner except that the material remaining after removal of the cyclohexane was distilled at one millimeter pressure. The distillate and remaining residue were dissolved in chloroform, and infrared spectra were obtained on each. A small peak in the nitrile region was observed in the infrared spectra of the distillate. Identification of the reaction products is being continued. The cyanogen consumed in this irradiation was 0.0110 mole, which compares very favorably with the 0.0113 mole consumed in the previous cyanogen-cyclohexane irradiation.

The cyanogen-benzene irradiation mixture from the stainless steel bomb was discarded as it was evident leakage had occurred. Dosimetry studies of the center hole with the stainless steel bomb in a brass holder gave a dose of 6.08×10^{19} ev/gm/hr.

Calibration of the gas chromatographic unit is progressing and will be continued. This method will be used in the future for the analysis of the gaseous radiolysis products.

During the coming month, attention will be given to: (a) further

irradiation in the stainless steel bomb, (b) further characterization of the radiolysis products, and (c) irradiations involving varying ratios of cyanogen to organic compound.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

February 28, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 7, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from February 1 to February 28, 1961

Gentlemen:

During the past month, six mixtures of cyanogen-cyclohexane have been irradiated. Further calibration work has been done with the gas chromatographic unit. A nitrogen analysis was obtained on a sample of high molecular weight radiolysis product from irradiated cyanogen-cyclohexane mixtures.

The cyanogen-cyclohexane irradiations (Nos. 29 to 34) were run for 24-hour intervals over a period of 24 to 144 hours. The irradiated mixtures were treated in the usual manner. The combined residues were distilled at 260°C and 2 mm pressure and gave a clear yellow distillate. The infrared spectrum of the distillate had a strong nitrile peak at 4.40 microns. The results of these irradiations are summarized in Table I.

TABLE I

IRRADIATIONS OF CYANOGEN-CYCLOHEXANE MIXTURES

Irradiation Mixture No.*	Period of Irradiation (Hours)	Cyanogen Charge (Moles)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
32	24	0.0072	0.0060	0.0012	1.1×10^{21}
29	48	0.0092	0.0058	0.0034	2.2×10^{21}
30	72	0.0085	0.0045	0.0040	3.8×10^{21}
31	96	0.0169	0.0124	0.0045	4.4×10^{21}
34	120	0.0030	0.0030	0.0048	6.4×10^{21}
33	144	0.0089	0.0026	0.0063	6.6×10^{21}

*In each irradiation, 0.232 mole of cyclohexane was used.

The combined residues from irradiations (Nos. 25 to 27) of cyanogen-cyclohexane were distilled (See Quarterly Technical Status Report No. 3, p.2). A nitrogen analysis (Clark Microanalytical Laboratory) on this material gave a value of 4.66 per cent.

Work with the gas chromatographic unit is being continued. It has not yet been possible to resolve cyanogen from a prepared mixture of hydrocarbon gases similar to a mixture of radiolysis products.

During the coming month, attention will be given to: (a) further irradiations in the stainless steel bomb and (b) further characterization of the radiolysis products.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

April 30, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 8, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from April 1 to April 30, 1961

Gentlemen:

During April, a cyanogen-cyclohexane mixture and samples of pure cyclohexane were irradiated. Calibration work with the gas chromatographic unit was continued. The annual report was completed.

Chromatographic analysis of the radiolysis products from the irradiations of cyclohexane and cyanogen-cyclohexane are currently underway. From work to date, it appears that a tetra-isobutylene chromatographic column will be satisfactory for analysis of the gaseous radiolysis products and that a Ucon oil LB-550-X column will be satisfactory for analysis of the heavier radiolysis products.

A calibrated gas-transfer apparatus has been fabricated to be used in transferring known and reproducible amounts of cyanogen in the preparation of mixtures for irradiations. In anticipation of conducting irradiations at other temperatures, the solubilities of cyanogen in several organic liquids at temperatures other than 25° C are being determined.

During the coming month, attention will be given to irradiations of mixtures of cyanogen-cyclohexane with variation of the concentration of cyanogen and total dose.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

May 31, 1961

U. S. Atomic Energy Commission
1717 H. Street N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 9, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from May 1 to May 31, 1961

Gentlemen:

During May, four mixtures of cyanogen-cyclohexane were irradiated, the gas-transfer apparatus was calibrated, and solubility determinations of cyanogen in organic liquids were continued.

The results of the above irradiations were inconclusive due to experimental difficulties encountered in the preparation of the samples for irradiation and in the analysis of the irradiated mixtures.

The gas-transfer apparatus for use with cyanogen has been calibrated and the results were checked by the usual titration procedure. The gas chromatographic work related to analysis of the irradiated mixtures is continuing.

During the coming month, emphasis will be placed on the irradiations of cyanogen-cyclohexane mixtures with variation in the total dose and with variation in the cyanogen-cyclohexane ratio at a constant dose.

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

Respectfully submitted,

James A. Knight, Jr.
Project Director

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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

July 31, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 10, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from July 1 to July 31, 1961

Gentlemen:

During July, four samples of cyclohexane were irradiated and used in the analysis of the radiolysis products by gas chromatography. Irradiated cyclohexane-cyanogen mixtures will be analyzed by gas chromatographic methods, and a comparison will be made of the results of irradiated cyclohexane and irradiated mixtures of cyclohexane-cyanogen.

Mr. Richard Stokes is a research assistant for three-fourths time on the project. He will devote the remainder of his time to academic work toward the M.S. degree. During the past month, he has gained experience in the laboratory procedures and experimental techniques utilized in this project.

During the coming month, emphasis will continue to be placed on the gas chromatographic analysis of irradiated cyclohexane and irradiated mixtures of cyclohexane-cyanogen.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
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Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

August 31, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 11, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from August 1 to August 31, 1961

Gentlemen:

During August, two samples of cyclohexane and one sample of cyclohexane-cyanogen were irradiated. These irradiated samples are in the process of being analyzed by gas chromatography.

After satisfactory analyses of irradiated cyclohexane and irradiated mixtures of cyclohexane-cyanogen are obtained, a comparison of the results will be made with an effort to suggest a possible mechanism for the radiation-induced cyanogenation of cyclohexane. Cyclohexane was selected for this phase of the work since a considerable amount of work has been reported on the radiation chemistry of pure cyclohexane.

Certain experimental difficulties are still being encountered in the preparation of mixtures of cyanogen and hydrocarbons for irradiation and in the gas sampling of the irradiated material for chromatographic analysis.

During the coming month, emphasis will continue to be placed on the gas chromatographic analysis of irradiated cyclohexane and irradiated mixtures of cyclohexane-cyanogen.

Respectfully submitted,

Approved:

R. C. Palmer
Co-Technical Director

James A. Knight, Jr.
Project Director

W. C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

October 31, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 12, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from October 1 to October 31, 1961

Gentlemen:

During October, five samples of cyclohexane were irradiated. These samples were irradiated for the purpose of analyzing the radiolysis products by gas chromatography. G-values obtained to date for radiolysis products from cyclohexane have been lower than values reported in the literature.

The dose rate in the sample holes of the Cs irradiator which are employed in this work were determined with the ferrous iron dosimeter. In so far as possible the same geometry was employed in the dose rate measurements as is used in the irradiation of samples. The dose rate in each of the three holes was found to be 3.8×10^{19} ev/gm-hr. This value is lower than previously reported values.

A sample of cyclohexyl cyanide was prepared from cyclohexanecarboxylic acid. The cyclohexyl cyanide is needed for identification and calibration work as it is one of the expected radiolysis products from irradiated cyanogen-cyclohexane mixtures.

During the coming month, emphasis will continue to be placed on the gas chromatographic analysis of irradiated cyclohexane and irradiated mixtures of cyclohexane-cyanogen.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

R. C. Palmer
Co-Technical Director

W. C. Whitley, Co-Technical Director and Chief,
Chemical Sciences Division

REVIEW
PATENT 11-7 19 61 BY
FORMAT 19 BY

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
November 30, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 13, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from November 1 to November 30, 1961

Gentlemen:

During November, several samples of cyclohexane were irradiated. These samples were irradiated for the purpose of analyzing for the major radiolysis products by gas chromatography. Reproducible G-values have been obtained for cyclohexene and dicyclohexyl.

A new gas-transfer apparatus was fabricated for use in the preparation of mixtures of cyanogen and organic compounds. This apparatus is being assembled for use in the coming month.

Cyanogen is now commercially available, and a small cylinder has been obtained. This material will be utilized in our future work.

During the coming month, emphasis will continue to be placed on the gas chromatographic analysis of irradiated cyclohexane and irradiated mixtures of cyclohexane-cyanogen.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

REVIEW
PATENT 12-18 1961 BY
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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

January 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 14, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from January 1 to January 31, 1962

Gentlemen:

During January, two samples of cyclohexane and two mixtures of cyclohexane and cyanogen were irradiated. These samples were irradiated for the purpose of analyzing for the major radiolysis products by gas chromatography.

Ucon oil LB-550X has been found to be a satisfactory column packing for the gas chromatographic analysis of cyclohexyl cyanide. The gas chromatographic unit has been calibrated for thermal response to cyclohexyl cyanide, utilizing solutions of cyclohexyl cyanide in cyclohexane.

Experimental difficulties are still being experienced in the quantitative determinations of the radiolytic gases from irradiated cyclohexane and irradiated mixtures of cyanogen and cyclohexane.

During the coming month, additional irradiations of cyclohexane and mixtures of cyclohexane and cyanogen will be made and emphasis will continue to be placed on the gas chromatographic analysis of the major radiolysis products from cyclohexane and cyanogen-cyclohexane mixtures.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

REVIEW
PATENT 2-7 1962 BY
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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

February 28, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 15, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from February 1 to February 28, 1962

Gentlemen:

During February, one sample of cyclohexane and three mixtures of cyclohexane and cyanogen were irradiated for the purpose of analyzing for the major radiolysis products by gas chromatography.

Four different gas chromatographic columns were tested for use in analyzing the gaseous mixture from irradiated mixtures of cyanogen-cyclohexane. The gaseous mixture might be expected to contain hydrogen, hydrogen cyanide, cyanogen, methane, ethane, ethylene, propane, and propylene, and an ideal column would be one which would resolve each of the components from one another. Of the columns tested and the conditions used, a 25-foot column of 20 per cent by weight of tri-m-cresyl phosphate is the most promising, although it is not ideal. Additional experimental work will be performed on this problem.

During the coming month, additional irradiations of cyclohexane and mixtures of cyclohexane and cyanogen will be made and emphasis will continue to be placed on the gas chromatographic analysis of the major radiolysis products from cyclohexane and cyanogen-cyclohexane mixtures.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

REVIEW
PATENT 6-7 1962 BY
FORMAT ✓ 19 1 BY DD

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
May 4, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 16, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from April 1 to April 30, 1962

Gentlemen:

During April the second annual report was completed and printed.

The gaseous mixture from irradiations of cyanogen-cyclohexane contain hydrogen, hydrogen cyanide, small quantities of hydrocarbon gases such as methane, and unreacted cyanogen. It is desirable to be able to analyze this mixture by gas chromatographic methods. An ideal solution would be a column which would resolve each of the components of the mixture from one another. The columns tested to date include a silica gel column, a 12-foot and a 25-foot tetraisobutylene column, a 12-foot and a 25-foot tri-m-cresyl phosphate column, and a 6-foot Carbowax column. Neither one of the columns tested proved satisfactory for analysis for all of the components of the gaseous mixture. The gaseous mixture can be analyzed by gas chromatography with three columns as follows: (1) hydrogen, methane, and other hydrocarbon gases on a silica gel column; (2) hydrogen cyanide on a 25-foot tetraisobutylene column; and (3) cyanogen on a 12-foot tri-m-cresyl phosphate column.

Two irradiations of pure cyclohexane were made to check the amounts of gases formed. The G values for a dose of 2.46×10^{20} ev/gm were 4.8 and 4.9. These values are in much better agreement than previous values with the literature G values for hydrogen from cyclohexane, which are in range of about 5.0 to 5.4.

During the coming month, additional irradiations of cyclohexane and mixtures of cyclohexane and cyanogen will be made and emphasis will continue to be placed on the gas chromatographic analysis of the major radiolysis products.

Respectfully submitted,

Approved:

James A. Knight, Jr.
Project Director

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

May 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 17, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from May 1 to May 31, 1962

Gentlemen:

During May attention was given to the preparation of a report presented at the Contractors' Meeting held at the Brookhaven National Laboratory on May 28 and 29, 1962. Additional irradiations of mixtures of cyanogen and cyclohexane were made for the purpose of analyzing for the major radiolysis products by gas chromatography.

G values for cyclohexyl cyanide for some irradiations have been obtained and are listed in Table I.

TABLE I

G VALUES FOR CYCLOHEXYL CYANIDE

Irradiation No.	Cyclohexane (Grams)	Cyanogen (Ml, S.T.P.)	Dose (ev/gm)	G
86	7.7	87	2.44×10^{20}	7.3
91	8.0	90	2.44×10^{20}	6.6
88	7.8	102	4.88×10^{20}	6.7
93	7.7	91	4.88×10^{20}	7.6

In rechecking some of the G values for cyclohexyl cyanide, it was found that the amount of cyclohexyl cyanide in the irradiated sample decreased with increasing time after irradiation. Therefore, two irradiations were made and analyzed for cyclohexyl cyanide as soon as possible after removal from the source and at varying intervals over a period of 35 days. It was found that the amount of cyclohexyl cyanide decreased with increasing time after

irradiation. The data are given in Table II, and the decrease is shown in terms of G values.

TABLE II

DECREASE IN CYCLOHEXYL CYANIDE
WITH TIME AFTER IRRADIATION

Time After Irradiation (Days)	G Values, Cyclohexyl Cyanide	
	Irradiation No. 86	Irradiation No. 88
1	7.5	6.9
3	6.8	---
10	4.5	4.2
24	2.3	2.3
29	2.1	2.0
35	1.7	1.7

During the coming month, additional irradiations of mixtures of cyanogen and cyclohexane will be made and emphasis will continue to be placed on the gas chromatographic analysis of the major radiolysis products.

Respectfully submitted,

James A. Knight, Jr.
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

July 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 18, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from July 1, to July 31, 1962

Gentlemen:

During July, Quarterly Technical Status Report No. 7 was completed and published.

Attention was given to additional work on the decrease of the amount of cyclohexyl cyanide in an irradiated mixture with increasing time after irradiation. Three samples from a mixture, irradiated for a total dose of 4.88×10^{20} ev/gm, were treated as follows. One portion was washed with water and dried with anhydrous magnesium sulfate. One portion was washed with 5 per cent hydrochloric acid, washed free of acid, and then dried with magnesium sulfate. One portion was washed with 5 per cent potassium hydroxide, washed free of base, and then dried with magnesium sulfate. Each sample was analyzed by gas chromatography for cyclohexyl cyanide immediately after treating as above and 12 days later. Exact quantitative analyses were not made, but on the basis of peak heights, the washing with potassium hydroxide gives a sample in which the amount of cyclohexyl cyanide decreases with time by only a small amount. Washing with water and 5 per cent hydrochloric acid did not have any desirable effects. Additional work is planned along these lines.

In order to determine if any cyclohexyl cyanide is reduced during the irradiation to detectable amounts of cyclohexylmethylamine, an authentic sample of cyclohexylmethylamine was prepared by reduction of cyclohexyl cyanide with lithium aluminum hydride. Gas chromatographic analysis at conditions under which cyclohexyl cyanide and cyclohexylmethylamine are resolved did not indicate the presence of any cyclohexylmethylamine in the irradiated sample. It was concluded that the cyclohexyl cyanide is not reduced during irradiation, or if reduction does occur, the quantity is too minute to be detected by our gas chromatographic analysis.

A new apparatus for the collecting and sampling of gases from irradiated mixtures has been fabricated. This equipment will be used in

efforts to obtain quantitative analysis of the gaseous mixtures from irradiated mixtures of cyanogen and cyclohexane.

During the coming month, attention will be given to additional work on the decrease in the amount of cyclohexyl cyanide with time and on the analysis of the gaseous mixtures from irradiated mixtures of cyanogen and cyclohexane.

Respectfully submitted,

James A. Knight, Jr.
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
August 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 19, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from August 1 to August 31, 1962

Gentlemen:

During August, five samples of mixtures of cyanogen and cyclohexane were irradiated. Due to breakage, three of the samples were not suitable for analysis.

The gaseous mixtures from the two irradiations were analyzed by gas chromatographic techniques for hydrogen, cyanogen and hydrogen cyanide. No hydrocarbon gases were detected by the gas chromatographic analysis under the conditions employed. Samples of the irradiated liquid were treated as mentioned in Progress Letter No. 18. The original irradiated liquid plus the treated samples are being analyzed at varying time intervals for cyclohexyl cyanide to determine the effect the various treatments have on the quantity of cyclohexyl cyanide. The data will be presented in the next report.

Mr. Richard Stokes, research assistant on this project, has resigned to continue his education at another institution. Since the project is not to be renewed beyond October 31, 1962, it will not be feasible to replace him.

During the coming month, attention will be given to completing the laboratory work in progress and preparing the final report.

Respectfully submitted,

James A. Knight, Jr.
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

October 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 20, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from October 1 to October 31, 1962

Gentlemen:

During October, Quarterly Technical Status Report No. 8 was completed and published.

Two samples of mixtures of cyanogen and cyclohexane were prepared for irradiation but broke after sealing and prior to irradiation.

Preparation of the final report has been initiated.

During the coming month, attention will be given to completing portions of the laboratory work and continuing preparation of the final report.

Respectfully submitted,

James A. Knight, Jr.
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

November 30, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 21, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from November 1 to November 30, 1962

Gentlemen:

During November, one sample of a mixture of cyanogen-cyclohexane was irradiated. Analysis of the sample is in progress. Preparation of the final report is in progress.

During the coming month, attention will be given to completing portions of the laboratory work and continuing preparation of the final report.

Respectfully submitted,

James A. Knight, Jr.
Project Director

QUARTERLY TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
1 MAY 1960 TO 31 JULY 1960
Printed 10 August 1960

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed By
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
1 MAY 1960 TO 31 JULY 1960
Printed 10 August 1960

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed By
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During this quarter, emphasis has been placed upon procurement of the necessary equipment, apparatus, chemicals, the preparation and handling of cyanogen, $(CN)_2$, and solubility determination of cyanogen in benzene. An acceptable analytical procedure for determining the amount of cyanogen dissolved in an organic liquid has been developed. A study of suitable tubing for chromatographic columns for use with cyanogen has been initiated. Irradiations of the cyanogen-benzene system are now being planned.

TABLE OF CONTENTS

This report contains 7 pages.

I. INTRODUCTION

This report summarizes the work performed from May 1, 1960, to July 31, 1960. The purpose of the research work under this contract is the study of radiation-induced cyanogenation of organic compounds, with interest not only in the products of the reactions, but also in the mechanism of the reactions.

During the past quarter, emphasis was placed on becoming familiar with the preparation and properties of cyanogen and the development of an accurate analytical method for determining the amount of cyanogen dissolved in an organic liquid.

Due to the toxic nature of cyanogen, all operations involving the preparation and handling of cyanogen are well-planned and carried out in a well-ventilated hood.

The director of this investigation is Dr. James A. Knight, Jr. Mr. Coleman Bryan, employed June 1, 1960, is a research assistant and is devoting full-time to the investigation.

II. EXPERIMENTAL WORK

A. Preparation and Handling of Cyanogen

After examination of various methods for the synthesis of cyanogen, the method employed by Janz[1] was selected as being the most suitable. This method consists of treating dry copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) with an excess of a saturated solution of sodium cyanide. The preparation is carried out in an all-glass apparatus in a well-ventilated hood. The rate of evolution of cyanogen is controlled by carefully regulating the addition of the saturated solution of sodium cyanide. During the preparation of cyanogen, the apparatus is continuously swept with nitrogen. The gases are bubbled through

[1] G. Janz, Inorganic Synthesis, edited by T. Moeller, McGraw-Hill Co., Inc., New York, N. Y. (1957), Vol. V, p. 43.

silver nitrate solution to remove any hydrogen cyanide and then passed through two drying towers of phosphorous pentoxide supported on glass wool. The cyanogen is condensed in a cold trap in a dry ice-acetone bath. The exit gases from the cold trap bubble through a potassium hydroxide solution which removes any remaining cyanogen. The yields of approximately 40 per cent agree with those reported by Janz.

B. Quantitative Determination of Cyanogen

It has been reported that cyanogen reacts quantitatively with sodium hydroxide or potassium hydroxide solutions to yield the alkali cyanide and cyanate.[2] This reaction forms the basis of the method for the quantitative determination of cyanogen. The cyanogen is reacted with an excess of 1 M potassium hydroxide solution and the potassium cyanide formed is then titrated with standard silver nitrate solution to the first permanent turbidity. The addition of a small quantity of potassium iodide gives a sharper end-point.

C. Transferring Cyanogen

The preferred method for transferring cyanogen is distillation by use of cold traps in an all-glass apparatus. This method is time-consuming as approximately 3 hours are required to transfer 0.5 g. The method now being employed is one of direct transfer with a spatula cooled to dry ice-acetone temperature. This method has proven satisfactory and is very time-saving.

D. Solubility of Cyanogen

Several different methods for dissolving cyanogen in benzene have been investigated. The first consisted of freezing benzene in a dry ice-acetone

[2] F. H. Rhodes, J. Ind. and Eng. Chem. 4, 652 (1912).

trap, distilling the cyanogen into the trap, sealing the trap, and allowing the mixture in the trap to warm to room temperature. After equilibration with occasional shaking for 4 hours, the cyanogen was then extracted with potassium hydroxide solution and titrated with silver nitrate. With this method only 0.61 ml at standard temperature and pressure of cyanogen dissolved per milliliter of benzene. The reported value is 28 ml at standard temperature and pressure of cyanogen per milliliter of benzene at 20° C.[3]

The next method tried was to bubble the cyanogen through liquid benzene. This was tried with both a capillary tube and a fritted glass disc. The capillary tube method gave a solution of 1.6 ml cyanogen per milliliter of benzene, while the fritted glass disc method gave 8.1 ml cyanogen per milliliter of benzene.

However, the procedure which has met with the greatest success is that of transferring solid cyanogen on a cold spatula to a tube in a dry ice bath, adding frozen benzene, stoppering the tube, and allowing the tube to warm up, occasionally releasing the pressure. Several different variations of this technique have been tried. The procedure in use now is as follows: The solid cyanogen is transferred to a tube in a dry ice-acetone bath and then frozen benzene is added. The mixture is placed in a water bath at 6° to 7° C and allowed to equilibrate. After equilibration at 7° C, the excess pressure is released, and the mixture is allowed to equilibrate at room temperature until no further pressure builds up. The cyanogen is then extracted and titrated. The amount of cyanogen dissolved in benzene by this technique was found to be 25 ml at standard temperature and pressure of cyanogen per milliliter of benzene.

[3] M. Berthelot, Ann. Chim. Phys. (8), 3, 146 (1904).

E. Irradiation Tube and Holder

An irradiation tube and a brass irradiation tube-holder have been designed and fabricated (Figure 1). The reaction tube is glass and of sufficient size to allow for possible vaporization of cyanogen during irradiation. During an irradiation the tube will be sealed. The cap of the brass tube-holder has an exhaust tube so that the brass tube-holder can be evacuated continuously during an irradiation. In the event of breakage of the glass irradiation tube, this will prevent the release of any gaseous substances in the laboratory. The brass tube-holder would also contain liquid resulting from breakage of the glass irradiation tube. One end of a 15-foot section of airplane cable for raising and lowering the brass tube-holder is soldered into the cap. In addition, the brass tube-holder will contain a thermocouple so that the temperature can be monitored during an irradiation.

F. Dosimetry Studies

Dosimetry studies were made with an irradiation tube in the brass tube-holder such that the same geometry was obtained that will be used in the actual irradiations. The ferrous ion dosimeter was employed, and measurements were made in outside sample tube No. 12 of the cesium-137 irradiator. The dose was found to be $(8.89 \pm 0.09) \times 10^5$ rad/hr.

III. DISCUSSION

Due to the extreme toxicity of cyanogen, careful attention has been given to the procedures, apparatus, and equipment to be used in the preparation and handling of cyanogen so that hazards will be reduced to a minimum. All preparations and the handling of cyanogen are carried out in a well-ventilated hood. The irradiation glass tube will be sealed and contained in a brass

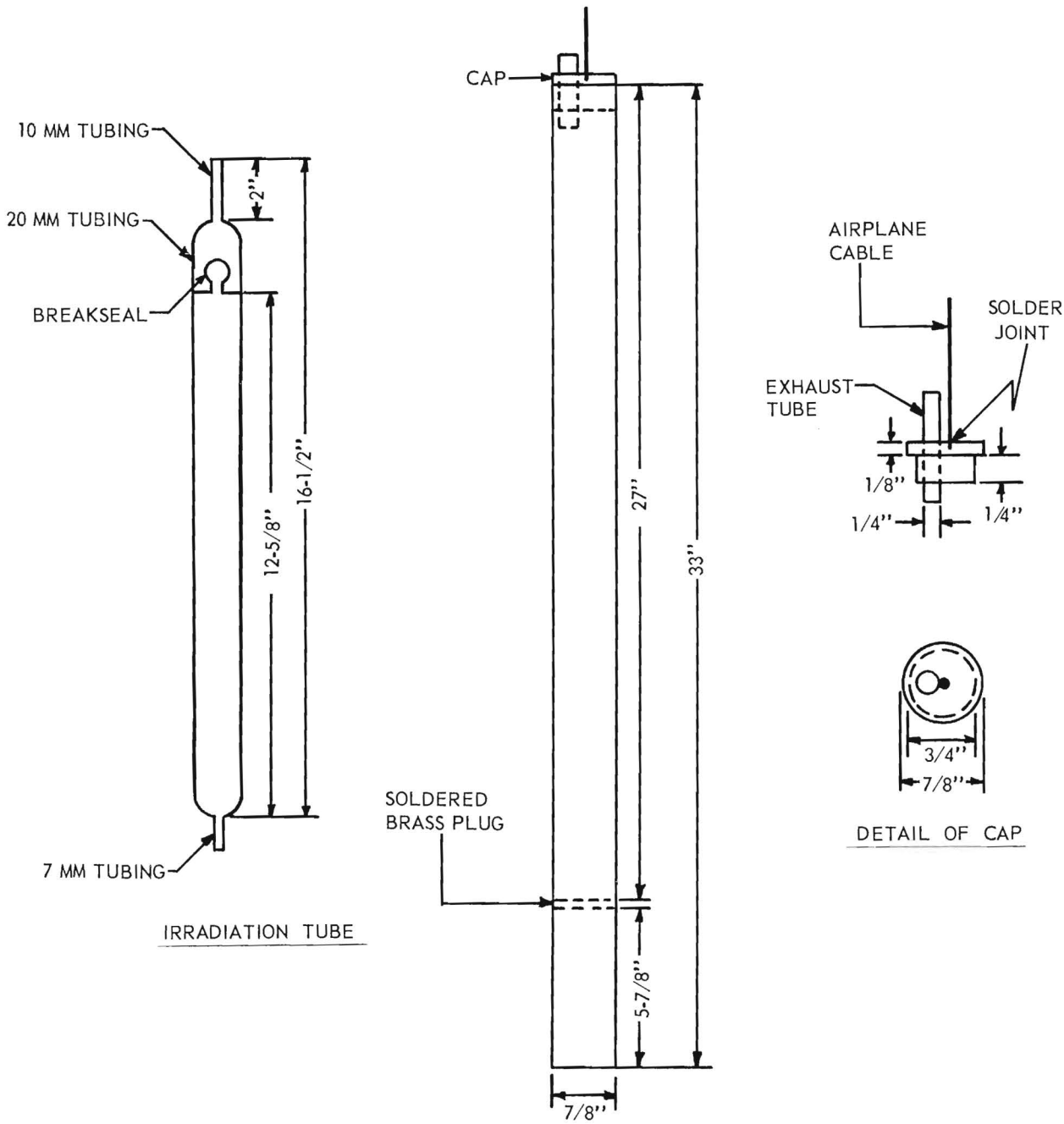

Figure 1. Irradiation Tube and Holder.

irradiation tube-holder during the irradiations in the cesium-137 irradiator. The brass tube-holder is designed so it will be continuously evacuated during an irradiation. In the event of breakage, gaseous material would therefore be evacuated and exhausted to a hood. Also, any spillage of liquid would be confined to the brass tube-holder.

Satisfactory methods and procedures have been worked out for dissolving cyanogen in organic liquids and for determining quantitatively the amount of dissolved cyanogen. To date, the solubility studies have been confined to benzene. The solubility studies will be extended to other hydrocarbons as required.

IV. SUMMARY

Several preparations of cyanogen were made and experience was gained in the handling of cyanogen. Several methods for dissolving cyanogen in benzene were investigated with the adoption of a method which gives 25 ml at standard temperature and pressure of cyanogen per milliliter of benzene. An irradiation tube and irradiation tube-holder, incorporating certain safety factors, were designed and fabricated. Dosimetry studies, employing the same geometry to be used in the irradiations, gave a dosage of $(8.89 \pm 0.09) \times 10^5$ rad/hr.

V. FUTURE PROGRAM

The immediate program will be directed toward: (a) carrying out irradiations of the cyanogen-benzene system, and (b) analysis of the products. The solubility of cyanogen in other hydrocarbons will be determined as required.

Respectfully submitted:

James A. Knight
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

QUARTERLY TECHNICAL STATUS REPORT NO. 2

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
1 AUGUST 1960 TO 31 OCTOBER 1960
Printed 10 November 1960

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed By
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY TECHNICAL STATUS REPORT NO. 2

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
1 AUGUST 1960 TO 31 OCTOBER 1960
Printed 10 November 1960

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed By
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During this quarter, emphasis has been placed on the irradiation of a number of cyanogen-organic mixtures and analysis of the irradiated mixtures, primarily for presence of cyano products. The organic compounds that have been irradiated in admixture with cyanogen are: benzene, toluene, n-heptane, cyclohexane, and 2,2,4-trimethylpentane. From infrared analysis of the irradiated mixtures, there is evidence that radiation-induced cyanogenation has occurred with toluene, n-heptane, cyclohexane, and 2,2,4-trimethylpentane. There is no indication that radiation-induced cyanogenation occurred with benzene under the conditions employed.

In order to carry out irradiations at higher concentrations of cyanogen, and consequently higher pressures, careful consideration has been given to the use of a stainless steel bomb with appropriate fittings. This equipment is presently being procured.

Solubility determinations of cyanogen in a number of organic compounds to be used in irradiations have been made. Attention is being given to various materials that can be used for chromatographic packings and columns with cyanogen.

TABLE OF CONTENTS

This report contains 8 pages.

LIST OF TABLES

I. INTRODUCTION

This report summarizes the work performed from August 1, 1960, to October 31, 1960. The purpose of the research work under this contract is the study of radiation-induced cyanogenation of organic compounds, with interest not only in the products of the reaction, but also in the mechanism of the reactions.

During the past quarter, a total of 17 irradiations were made as follows: (a) 11 on mixtures of cyanogen-organic compounds; (b) 5 on pure organic compounds; and (c) 1 on pure cyanogen. Infrared spectra were obtained on the distillates and flask residues of each irradiation, except pure cyanogen, and the differences in the spectra of the samples from the irradiated cyanogen-organic mixtures and the irradiated organic compounds were examined. From the infrared spectra there is evidence that radiation-induced cyanogenation has occurred with toluene, n-heptane, cyclohexane, and 2,2,4-trimethylpentane. There is no indication that radiation-induced cyanogenation of benzene occurred under the conditions employed.

The solubility of cyanogen in benzene, toluene, cyclohexane, n-heptane, 2,2,4-trimethylpentane, and 2,4,4-trimethylpentene-1 at 25.0° C has been determined.

II. EXPERIMENTAL WORK

A. Irradiation of Cyanogen-Organic Mixtures

The cyanogen-organic mixtures for irradiation were prepared by weighing the reaction tube, introducing a known amount of the organic compound into the glass reaction tube at dry ice-acetone bath temperatures, adding the cyanogen to the organic compound, sealing of the reaction tube, and again

weighing the reaction tube after the contents have reached room temperature. The weight of cyanogen added was then determined. The reaction tube was then placed in a brass irradiation tube holder fitted with an exhaust tube and thermocouple, and the whole assembly placed in the Cesium-137 Irradiator.

The amount of cyanogen remaining after irradiation was determined by the usual method of extraction and titration. The organic phase was then dried with magnesium sulfate, filtered, and distilled. Infrared spectra were obtained on both the flask residue and the distillate, and the spectra were examined for nitrile and amine absorption bands.

The organic compounds investigated thus far in admixture with cyanogen are benzene, toluene, cyclohexane, n-heptane, and 2,2,4-trimethylpentane. Infrared absorption at 4.4 microns, which is attributed to the nitrile radical, has been observed for the flask residues for all of the above organic compounds except benzene. In addition to the nitrile absorption at 4.4 microns, the infrared spectra of the flask residues of irradiations Nos. 10, 11, 12, and 15 showed absorption at 2.92 which could be attributed to the presence of an amine grouping.

The results of the irradiations of the cyanogen-organic mixtures are summarized in Table I, and the comments on the infrared spectra are given in Table II.

B. Dosimetry Studies

Additional dosimetry studies were made in the outside sample tubes, Nos. 1 and 11, of the Cesium-137 Irradiator. These studies were made in a glass reaction tube encased in a brass irradiation tube holder so marked that the tube holder for each sample hole may be readily identified and used only in

TABLE I

IRRADIATIONS OF CYANOGEN-ORGANIC MIXTURES

Irradiation Mixture Number	Organic Compound (Moles)	Cyanogen (Moles)	Period of Irradiation (Hours)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
1	Benzene 0.11	0.0052	3	0.0022	0.0030	1.6×10^{20}
3	Benzene 0.11	0.0097	8	0.0041	0.0056	4.2×10^{20}
4	Benzene 0.11	0.0102	7	0.0052	0.0050	3.6×10^{20}
6	Benzene 0.255	0.0174	18	----[a]	----	9.5×10^{20}
7	Toluene 0.246	0.0352	24	0.0067	0.0285	1.3×10^{21}
8	n-Heptane 0.171	0.0308	72	0.0115	0.0193	3.8×10^{21}
9	Benzene 0.275	0.0242	163	0.0202	0.0040	8.6×10^{21}
10	n-Heptane 0.171	0.0065	168	0.0030	0.0035	8.9×10^{21}
11	Toluene 0.235	0.0119	168	0.0027	0.0093	7.7×10^{21}
12	Cyclohexane 0.232	0.0116	168	0.0003	0.01131	8.9×10^{21}
15	2,2,4-trimethylpentane 0.152	0.0164	168	0.0132	0.0032	8.9×10^{21}

[a] It was not possible to titrate this sample due to the black color of the potassium hydroxide phase.

TABLE II

COMMENTS ON INFRARED SPECTRA

Irradiation No.	Distillate	Residue in Flask
1	Very similar to pure benzene	Identical with flask residue of irradiated benzene
3	Very similar to pure benzene	Identical with flask residue of irradiated benzene
4	Very similar to pure benzene	Identical with flask residue of irradiated benzene
6	Identical to pure benzene	Identical with flask residue of irradiated benzene
7	Very similar to pure toluene	No nitrile peak observed
8	Identical to pure n-heptane	Possible nitrile peak at 4.4 microns
9	Identical to pure benzene	Identical with flask residue of irradiated benzene
10	Very similar to pure n-heptane	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns
11	Very similar to pure toluene	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns
12	Very similar to pure cyclohexane	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns
15	Very similar to pure 2,2,4-trimethylpentane	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns

that sample hole. The ferrous ion dosimeter was employed. Measurements in outside sample hole No. 1 showed a dose of $(7.59 \pm 0.12) \times 10^5$ rad/hr. and in outside sample hole No. 11, a dose of $(7.62 \pm 0.15) \times 10^5$ rad/hr. Outside sample hole No. 12 was previously found to have a dose of $(8.89 \pm 0.09) \times 10^5$ rad/hr.

C. Quantitative Determination of the Solubility of Cyanogen in Organic Compounds

The solubility studies were made in a tube (4.2 cm x 10.5 cm) fitted with a ground glass cap (45/50 standard taper) to which a stopcock and U-manometer were attached.

In the determination of the solubility of cyanogen in an organic compound, the organic compound was placed in the solubility apparatus which was at dry ice-acetone temperature. The cyanogen was transferred as a solid to the apparatus, and the mixture was allowed to equilibrate partially at 5 to 7° C in a water bath. The mixture was then placed in a constant temperature bath at 25.0° C and allowed to equilibrate until there was no pressure build-up as indicated by the mercury U-manometer. The cyanogen was then determined by the previously reported method of extracting the cyanogen with aqueous potassium hydroxide and titrating, with standard silver nitrate, the potassium cyanide formed. The solubilities are reported in milliliters of cyanogen at standard temperature and pressure per milliliter of organic compound and are summarized in Table III.

TABLE III

SOLUBILITY OF CYANOGEN IN ORGANIC LIQUIDS AT 25.0° C

Compound	Mole Cyanogen/10 ml Organic	ml Cyanogen/ml Organic
Benzene	0.0144	32.2 ± 0.6
Toluene	0.0156	35.0 ± 0.2
Cyclohexane	0.0079	17.7 ± 0.2
n-Heptane	0.0091	20.4 ± 0.2
2,4,4-Trimethyl-pentene-1	0.0105	23.5 ± 0.1
2,2,4-Trimethyl-pentane	0.0091	20.4 ± 0.4

III. DISCUSSION

Several representative hydrocarbons, benzene, toluene, n-heptane, 2,2,4-trimethylpentane, and cyclohexane, have been irradiated in admixture with cyanogen. The conditions and results of the irradiations are summarized in Tables I and II. The gross reaction products have been analyzed by infrared spectra primarily to determine if any cyano products were present. The infrared spectra of the gross reaction products from the irradiated mixtures of toluene, n-heptane, 2,2,4-trimethylpentane, and cyclohexane showed an absorption band at 4.4 microns which is attributed to the cyano group (-CN). The infrared spectra for the samples irradiated for 168 hours (irradiation Nos. 10, 11, 12, and 15, Table I) also showed an absorption peak at 2.92 microns which can be attributed to an amine group. The absorption at 4.4 microns indicated very strongly that radiation-induced cyanogenation has taken place with toluene, n-heptane, 2,2,4-trimethylpentane, and cyclohexane.

The absorption at 2.92 microns for these samples indicates that the amine group is also present. The presence of the amine group suggests that some of the cyano product has been reduced to the amine during the irradiation. None of the infrared spectra of the gross reaction products from any of the irradiations of benzene showed an absorption band at 4.4 microns. This indicates that under the conditions employed no radiation-induced cyanogenation occurred with benzene.

The amounts of cyanogen that have been used in the irradiations to date have been limited by: (a) the solubilities of the cyanogen in the hydrocarbons, and (b) the use of glass irradiation tubes, which will not withstand high pressures. For these reasons, careful consideration has been given to the use of a stainless steel bomb with appropriate fittings as an irradiation tube. The use of this equipment should permit higher molar ratios of cyanogen to hydrocarbon to be irradiated. The stainless steel bomb and appropriate fittings are in the process of being procured.

The solubilities of cyanogen in the hydrocarbons used in the irradiations have been determined at 25.0° C. This information was needed to determine the amounts of cyanogen that could be mixed with the hydrocarbon and safely irradiated. From the data, cyanogen shows increasing solubility in the classes of hydrocarbons in the following order: cycloalkanes, alkanes, alkenes and aromatics.

IV. SUMMARY

Seventeen irradiations have been completed in the past quarter. These irradiations consisted of 11 of cyanogen-hydrocarbon mixtures, 5 of pure hydrocarbons, and 1 of pure cyanogen. The infrared spectra of the gross reaction products from toluene, n-heptane, 2,2,4-trimethylpentane and cyclohexane had

absorption bands at 4.4 microns and at 2.92 microns, which can be attributed to the presence of the cyano group and an amine group respectively. The absorption at 4.4 microns (cyano group) is evidence that radiation-induced cyanogenation has taken place with these hydrocarbons. Under the conditions employed, there is no evidence that any cyano products were formed with benzene.

The solubilities of cyanogen in the hydrocarbons used in the irradiations have been determined. The solubility of cyanogen in the various classes of hydrocarbons shows increases in the following order: cycloalkanes, alkanes, alkenes, and aromatics.

Dosimetry studies, employing the same geometry as used in the irradiation have been made with the ferrous ion dosimeter in holes Nos. 1, 11, and 12 of the Cesium-137 Irradiator. The doses for the holes were found to be: (a) No. 1, $(7.59 \pm 0.12) \times 10^5$ rad/hr.; (b) No. 11, $(7.62 \pm 0.15) \times 10^5$ rad/hr.; and (c) No. 12, $(8.89 \pm 0.09) \times 10^5$ rad/hr.

V. FUTURE PROGRAM

The immediate program will be directed toward: (a) irradiations in a stainless steel reaction bomb so that higher molar ratios of cyanogen to hydrocarbon can be employed with particular emphasis on the benzene-cyanogen system; (b) irradiations of cyanogen with some other selected hydrocarbons; and (c) further characterization of the cyano products from the irradiated mixtures by the use of gas chromatography and other methods.

Approved:

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QUARTERLY TECHNICAL STATUS REPORT NO. 3

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
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Placed By
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SAVANNAH RIVER OPERATIONS OFFICE
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Performed for
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OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During this quarter, emphasis has been placed on the irradiation of a number of cyanogen-organic mixtures and analysis of the irradiated mixtures for cyano products. The organic compounds that have been irradiated in admixture with cyanogen are: 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, benzene and cyclohexane. From infrared analysis of the irradiated mixtures, there is evidence that radiation-induced cyanogenation has occurred with all of the above organic compounds.

A stainless steel reaction bomb was obtained and utilized in an irradiation of a cyanogen-benzene mixture in a mole ratio of 1 to 3. Infrared analysis of the radiolysis products indicates that cyanogenation occurred during the irradiation.

A gas chromatographic unit has been obtained. Testing of column packings and calibration work is in progress. This unit will be utilized in the analysis and characterization of the radiolysis products.

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LIST OF TABLES

This report contains 7 pages.

I. INTRODUCTION

This report summarizes the work performed from November 1, 1960, to January 31, 1961. The purpose of the research work under this contract is the study of radiation-induced cyanogenation, with interest not only in the products of the reaction, but also in the mechanism of the reactions.

During the past quarter, a total of 13 irradiations were made as follows: (a) Nine on mixtures of cyanogen-organic compounds, and (b) Four on pure organic compounds. From the infrared spectra there is evidence that radiation-induced cyanogenation has occurred with all the organic compounds irradiated in admixture with cyanogen.

Two blank runs, cyanogen-n-heptane and cyanogen-2,4,4-trimethylpentene-1, were made in which the cyanogen-hydrocarbon mixtures were sealed in reaction tubes and allowed to sit at room temperature for 168 hours. These experiments were carried out to establish if any reaction would occur in the absence of high energy radiation.

II. EXPERIMENTAL WORK

A. Irradiation of Cyanogen-Hydrocarbon Mixtures

The cyanogen-hydrocarbon mixtures for irradiation were prepared by weighing the reaction tube, introducing a known amount of organic compound into the glass reaction tube at dry ice-acetone temperatures, adding the cyanogen to the organic compound, sealing the reaction tube, and again weighing the reaction tube after the contents have reached room temperature. The reaction tube was then placed in a brass irradiation tube holder fitted with an exhaust tube, and the whole assembly placed in the Cesium-137 Research Irradiator.

The amount of cyanogen remaining after irradiation was determined by the usual method of extraction and titration. The organic phase was then dried over magnesium sulfate, filtered and distilled. Infrared spectra were obtained on both the flask residue and the distillate.

A stainless steel bomb was obtained so that mixtures with larger ratios of cyanogen to organic compounds could be irradiated. One irradiation with a molar ratio of cyanogen to benzene of one to three was carried out as follows: The bomb was charged by generating cyanogen directly into the bomb, carefully adding a known weight of benzene at dry ice-acetone temperatures and then sealing with a brass valve. The bomb was then weighed at room temperature, sealed in a brass holder fitted with an exhaust valve and thermocouple, and placed in the Cesium-137 Research Irradiator. The irradiated contents of the bomb were treated similarly to other irradiated mixtures.

Several cyanogen-cyclohexane mixtures were irradiated with a constant weight of cyclohexane and varying amounts of cyanogen. The flask residues of these irradiations were combined and redistilled from a special apparatus at 260° C and 2 mm pressure. The distillate, 0.3275 gram, showed a strong nitrile peak at 4.40 microns while the flask residue gave no peak.

The results of the cyanogen-organic mixtures are summarized in Table I and the comments on the infrared spectra are given in Table II.

B. Dosimetry Studies

An additional dosimetry study was made on the center hole of the Cesium-137 Research Irradiator. This study was made in a stainless steel bomb encased in a brass holder. The ferrous ion dosimeter was employed. Measurement in the center hole with this experimental setup showed a dose of $(1.01 \pm 0.01) \times 10^{6}$ rad/hr.

TABLE I

IRRADIATIONS OF CYANOGEN-ORGANIC MIXTURES

Irradiation Mixture No.*	Organic Compound (Moles)	Cyanogen (Moles)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
12	Cyclohexane (0.232)	0.0116	0.0003	0.0113	8.89×10^{21}
19	2,4,4-Trimethylpentene-1 (0.150)	0.0306	0.0227	0.0079	8.89×10^{21}
21	2-Methylpentane (0.206)	0.0220	0.0127	0.0093	8.89×10^{21}
22	3-Methylhexane (0.172)	0.0298	0.0200	0.0098	7.65×10^{21}
23	Benzene (0.225)	0.0078	0.0006	0.0072	1.02×10^{22}
24	Cyclohexane (0.232)	0.0167	0.0057	0.0110	8.89×10^{21}
25	Cyclohexane (0.232)	0.0147	0.0035	0.0112	7.65×10^{21}
26	Cyclohexane (0.232)	0.0297	0.0056	0.0240	8.89×10^{21}
27	Cyclohexane (0.232)	0.0045	0.0004	0.0041	7.68×10^{21}
28	Benzene (0.225)	0.0784	0.0404	0.0380	1.02×10^{22}

*All irradiations were carried out for a period of 168 hours. All irradiations except No. 28 were performed in glass irradiation tubes. Irradiation No. 28 was performed in a stainless steel bomb.

TABLE II

COMMENTS ON INFRARED SPECTRA

Irradiation No.	Distillate	Residue in Flask
19	Identical to pure 2,4,4-trimethylpentene-1	Possible nitrile peak at 4.4 microns
21	Very similar to pure 2-methylpentane	Possible nitrile peak at 4.4 microns
22	Very similar to pure 3-methylhexane	Possible nitrile peak at 4.4 microns
23	Identical to pure benzene	No nitrile peak observed
24	Very similar to pure cyclohexane	Possible nitrile peak at 4.4 microns
25-27	Very strong peak at 4.4 microns upon second distillation	No observable nitrile peak after second distillation
28	Identical to pure benzene	Possible nitrile peak at 4.4 microns

C. Blank Experiments

Two mixtures, cyanogen-n-heptane and cyanogen-2,4,4-trimethylpentene-1, were prepared in the same manner as for irradiation. These mixtures, after standing at room temperature for 168 hours, were treated in the same manner as an irradiated mixture. The cyanogen remaining indicates that no reaction took place in either case. Gas chromatographic analysis of the organic phase from each experiment showed only the pure compound present. Infrared curves of the organic phase did not show any absorption that could be attributed to the cyano group. The results are summarized in Table III.

TABLE III

BLANK EXPERIMENTS OF CYANOGEN-ORGANIC MIXTURES

Blank Experiment No.	Organic Compound	Cyanogen (Moles)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)
1	2,4,4-Trimethyl-pentene-1 (0.160)	0.0226	0.0225	0.0001
2	n-Heptane (0.171)	0.0280	0.0276	0.0004

III. DISCUSSION

Three additional organic compounds, 2,4,4-trimethylpentene-1, 2-methylpentane, and 3-methylhexane, have been irradiated in admixture with cyanogen. The conditions and results of these irradiations are given in Tables I and II. The gross radiolysis products which are higher boiling than the parent organic compound were analyzed by infrared spectra. The spectrum from each exhibited an absorption band at 4.40 microns which is attributed to the cyano group (-CN). This is strong evidence that radiation-induced cyanogenation occurred.

In all previous irradiations of mixtures of benzene and cyanogen, no evidence was obtained that any cyanogenation had occurred. With a stainless steel bomb, a mixture of cyanogen and benzene in a molar ratio of one to three was irradiated. This ratio of cyanogen to benzene was much higher than any used in previous irradiations. The infrared spectra of the gross radiolysis products which were higher boiling than benzene showed strong absorption at 4.40 microns. This infrared spectra compared very favorably with the infrared spectra of a

10 per cent benzonitrile in benzene solution, and very few of the characteristics of the infrared spectra of irradiated benzene were observed.

Several mixtures of cyanogen-cyclohexane with varying amounts of cyanogen were irradiated (Tables I and II). The cyanogen consumed in three of the irradiations was approximately the same (0.011 mole) even though the amount of cyanogen varied from 0.0116 to 0.0167 mole. In one irradiation, 0.0297 mole of cyanogen was used and 0.024 mole of cyanogen consumed. After removal of the cyclohexane from the irradiated mixtures, the flask residues, 1.426 gm, were combined and distilled at 260° C and 2 mm pressure. The distillate, 0.328 gm, was a clear yellow liquid showing a very strong cyano infrared absorption band at 4.40 microns. Absorption at 2.92 and 3.07 microns is possibly due to amine groups. The presence of these bands suggest that some reduction of the cyano product to an amine group occurs during irradiation.

The results of the two blank experiments showed that no reaction of cyanogen with either n-heptane or 2,4,4-trimethylpentene-1 occurred. The results of the blank experiments are given in Table III.

IV. SUMMARY

Thirteen irradiations have been completed in the past quarter. These irradiations consisted of nine cyanogen-organic mixtures and of four pure organic compounds. The infrared spectra of the gross reaction products of 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, and cyclohexane had absorption peaks at 4.4 and 2.92 microns, which can be attributed to the presence of the cyano group and an amine group respectively. At the increased cyanogen concentration in the cyanogen-benzene mixture, evidence from the infrared spectra indicated that cyanogenation had occurred.

Dosimetry of the center hole with the stainless steel bomb was found to be $(1.01 \pm 0.01) \times 10^6$ rad/hr.

V. FUTURE PROGRAM

The immediate program will be directed toward: (a) additional irradiation in the stainless steel bomb with higher concentrations of cyanogen, (b) irradiations of cyanogen with selected hydrocarbons, and (c) further characterization of the radiolysis products from the irradiated mixtures with infrared spectroscopy, gas chromatography and other applicable methods.

Respectfully submitted:

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Project Director

Approved:

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QUARTERLY TECHNICAL STATUS REPORT NO. 4

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
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AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During the past quarter, major emphasis was placed upon work directed toward the ultimate analysis by gas chromatography of the radiolysis products of the irradiated cyanogen-hydrocarbon mixtures. Several irradiations of cyclohexane and cyanogen-cyclohexane mixtures were made, and the gaseous radiolysis products were utilized in the development of sampling techniques for chromatographic analysis.

A gas-transfer apparatus was fabricated and calibrated for use in transferring known and reproducible amounts of cyanogen in the preparation of mixtures for irradiations.

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LIST OF TABLES

This report contains 5 pages.

I. INTRODUCTION

This report summarizes the work performed from April 1, 1961, to June 30, 1961. The purpose of the research work under this contract is the study of radiation-induced cyanogenation, with interest in both the cyano products and the mechanism of the reaction.

A detailed study of the radiation chemistry of the system cyanogen-cyclohexane is now underway with particular emphasis on the analysis of the radiolysis products. During the past quarter, several irradiations were made: eight on mixtures of cyanogen-cyclohexane and four on pure cyclohexane. The irradiated mixtures were utilized in the development of analytical procedures for the identification and quantitative determination of the major radiolysis products.

Mr. Coleman J. Bryan, who was a research assistant on this project for the past year, has completed his work for the M.S. degree. He has resigned in order to accept a position in industry. Mr. Richard Stokes, who received a B.S. degree from Emory University in June 1961, is now research assistant for three-fourths time on this project. He will devote the remainder of his time to academic work toward the M.S. degree.

II. EXPERIMENTAL WORK

A. Irradiation and Gas-Sampling of Cyanogen-Cyclohexane Mixtures and Cyclohexane

These mixtures were prepared by transferring known volumes of cyanogen gas in the gas-transfer apparatus to an irradiation tube containing cyclohexane at about -70° C. The tube was then sealed, placed in a brass tube-holder and irradiated for the desired time. After irradiation, the tube was sealed onto the all glass gas-sampling apparatus and the irradiated mixture cooled to about -70° C. The system was evacuated and the breakseal broken. The noncondensable gases were

pumped into a bulb for gas sampling. Samples for chromatographic analysis were taken through a rubber septum with a Hamilton microliter syringe. After noncondensable gases were sampled, the system was evacuated and the irradiated sample warmed to room temperature. Samples of the condensable gases were then taken for chromatographic analysis.

Gas samples of irradiated cyclohexane were obtained for chromatographic analysis in the same manner.

B. Gas Chromatographic Analysis

Two gas chromatographic units are employed in the analysis of the gaseous radiolysis products. One is used for the noncondensable gases and the other for condensable gases. An 8-foot column, packed with 30/60-mesh 13X molecular sieve, is used to analyze for noncondensable gases. A sample of the noncondensable gases showed only hydrogen was present. A 24-foot column, packed with 20 per cent by weight tricresyl phosphate on 30/60 Chromosorb, is employed for analysis of the condensable gases and some of the liquid products. A sample of the condensable gases gave, in addition to a peak for hydrogen, peaks corresponding to cyanogen and cyclohexane.

A sample of the irradiated liquid of the cyanogen-cyclohexane mixture showed three peaks in addition to those obtained from irradiated cyclohexane. One of these peaks corresponds to cyanogen and the other two have not been identified.

C. Purification of Cyclohexane

Gas chromatographic analysis of one of the best grades of commercial cyclohexane showed the presence of impurities. The cyclohexane was purified by distillation with a total condensation, intermittent take-off-type column. The packed section, 1-inch by 4-foot, was packed with Podbielniak Heli-Pak No. 2117

stainless steel packing. The take-off valve was operated by a solenoid and a 30-second cycle timer which was operated so that the valve was open one per cent of every 30-second cycle. Five-milliliter fractions were taken and the purity checked by gas chromatographic analysis. The impurities, however, were not completely removed by this careful fractional distillation, although the impurities were reduced to very small amounts. Approximately 800 ml of purified cyclohexane was obtained.

D. Solubility of Cyanogen in Organic Compounds

The solubility of cyanogen in several organic compounds at 40.0° C was determined in the manner described in Quarterly Technical Status Report No. 2, p. 5. The results are given in Table I.

TABLE I

SOLUBILITY OF CYANOGEN IN ORGANIC LIQUIDS AT 40.0° C

Compound	Mole Cyanogen/10 ml Organic	ml Cyanogen/ml Organic
Benzene	0.0030	6.7 ± 0.1
Toluene	0.0031	7.0 ± 0.2
Cyclohexane	0.0020	4.5 ± 0.1
n-Heptane	0.0024	5.1 ± 0.1
2,4,4-Trimethyl-pentene-1	0.0021	4.6 ± 0.1
2,2,4-Trimethyl-pentane	0.0022	4.9 ± 0.2

III. DISCUSSION

Twelve irradiations were made in the past quarter: four of pure cyclohexane and eight of cyanogen-cyclohexane mixtures. The irradiated material from these irradiations was utilized in developing experimental and sampling techniques for the gas chromatographic analysis of the radiolysis products. Hydrogen was identified as a product from irradiated cyclohexane and the cyanogen-cyclohexane mixtures. From the results to date there appears to be a smaller amount of hydrogen from the mixture than from the cyclohexane. The gas chromatographic analysis of the radiolysis products from cyclohexane and cyanogen-cyclohexane mixtures is continuing.

The commercial cyclohexane had some impurities present as shown by gas chromatographic analysis. The presence of these impurities could possibly affect the irradiation results and would interfere in the gas chromatographic analysis of the radiolysis products. These impurities, however, were not completely removed by careful fractional distillation of the cyclohexane. The impurities were reduced to very small amounts as shown by gas chromatographic analysis.

In anticipation of carrying out irradiations at higher temperatures, the solubility of cyanogen in a number of hydrocarbons at 40.0° C was determined. The solubility decreased to values in the range of one-fourth to one-fifth those obtained at 25.0° C for the same hydrocarbons. Due to the limited solubility of cyanogen in the hydrocarbons at 40.0° C, it appears doubtful if any irradiations can be conducted in glass irradiation tubes.

IV. SUMMARY

Considerable experience has been gained and certain experimental difficulties overcome in the program to analyze the radiolysis products by gas chromatography. The analysis by gas chromatography of the radiolysis products from cyclohexane

and cyanogen-cyclohexane is continuing on both a qualitative and a quantitative basis.

V. FUTURE PROGRAM

The immediate program will be directed toward the gas chromatographic analysis of the radiolysis products from cyclohexane and cyanogen-cyclohexane mixtures on both a qualitative and quantitative basis.

Respectfully submitted:

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QUARTERLY TECHNICAL STATUS REPORT NO. 5

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

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COVERING THE PERIOD
1 JULY 1961 to 30 SEPTEMBER 1961
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AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF ISOTOPE DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During the past quarter major emphasis has been placed on: (1) refinement of techniques for preparation of samples for irradiation and for sampling of radiolysis gases; and (2) utilization of gas chromatography as a method of analysis of the radiolysis products of irradiated cyclohexane and cyclohexane-cyanogen systems. A great deal of the work was devoted to analysis of irradiated cyclohexane for comparison with published results on irradiated cyclohexane.

The irradiation tube was redesigned and a gas-transfer apparatus was fabricated and calibrated for measurements of gaseous radiolysis products.

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This report contains 4 pages.

I. INTRODUCTION

This report summarizes the work performed from July 1, 1961, to September 30, 1961. The purpose of the research work under this contract is the study of radiation-induced cyanogenation, with interest in both the cyano products and the mechanism of the reaction.

Mr. Richard Stokes, who received a B.S. degree from Emory University in June 1961, is now research assistant for three-fourths time on this project. He will devote the remainder of his time to academic work toward the M.S. degree.

A detailed study of the radiolysis products from irradiated cyclohexane and cyclohexane-cyanogen systems is now underway. Particular emphasis is being placed on obtaining quantitative results from which G values can be calculated. During the quarter, several irradiations were made: two on mixtures of cyclohexane and cyanogen and twelve on pure cyclohexane. The irradiated samples were utilized in the improvement and refinement of techniques and procedures leading to the quantitative determination of the major radiolysis products.

II. EXPERIMENTAL WORK

A. Irradiation and Gas-Sampling of Cyclohexane and Cyanogen-Cyclohexane Mixtures

The pure cyclohexane samples were prepared by successively repeating several times the cycle of freezing (-70° C), evacuation, and melting in a helium atmosphere. The samples were sealed under vacuum and irradiated for the desired time. Cyclohexane for the mixtures was prepared as described above. Gaseous cyanogen was then transferred to the tube containing the cyclohexane (-70° C),

and the tube was sealed.

After irradiation, the tube was sealed onto the all-glass gas-sampling apparatus, and the irradiated sample cooled to -70° C. The system was evacuated and the break-seal broken. The noncondensable gases were pumped into a bulb for measurement and gas sampling. Samples for chromatographic analysis were taken through a rubber septum with a Hamilton microliter syringe. After the noncondensable gases were sampled, the system was evacuated and the irradiated sample was allowed to warm to room temperature. Samples of the gases, volatile at room temperature, were taken in the above manner.

The irradiated liquid was fractionally distilled and each fraction analyzed for the major radiolysis products by gas chromatography.

B. Gas Chromatographic Analysis

Two gas chromatographic units are being employed in the analysis of the radiolysis products. A 12-ft. column, packed with 30-60 mesh 13-X molecular sieve, is used to analyze the noncondensable gases. Samples of noncondensable gases show only hydrogen as being present. A 12-ft. column, packed with 20 per cent by weight tricresyl phosphate on 30-60 Chromosorb, is employed for analysis of some of the condensable gases and some of the liquid radiolysis products. Samples of the condensable gases have shown the presence of cyanogen (from mixtures) and some of the hydrocarbon gases. Analysis of the liquid products on the above column has shown the presence of cyclohexene. The liquid products boiling over 82° C are analyzed with a 15-ft. column packed with 20 per cent, by weight, Kel-F on 30-60 mesh Chromosorb. Dicyclohexyl has been identified in this manner.

III. DISCUSSION

Fourteen irradiations were made in the past quarter; twelve of pure cyclohexane and two of cyanogen-cyclohexane mixtures. The irradiated materials were utilized in refining experimental and sampling techniques for gas chromatcgraphic analysis of the radiolysis products. Hydrogen, ethane, propane, propylene, butane, butene-1, cyclohexene, and dicyclohexyl have been qualitatively identified from both cyclohexane-cyanogen and pure cyclohexane systems. Efforts are presently underway to obtain quantitative measurements of these products. When satisfactory quantitative experimental data on irradiated cyclohexane and cyanogen-cyclohexane have been obtained, a comparison will be made of the radiation chemistry of these two systems.

IV. SUMMARY

Considerable experience has been gained in the effort to achieve quantitative measurements as well as qualitative identification of the radiolysis products from cyclohexane and mixtures of cyanogen-cyclohexane. More refinements are needed for satisfactory quantitative results, and work is in progress toward this goal.

V. FUTURE PROGRAM

The immediate program will be directed toward a continuation of the gas chromatographic analysis of the radiolysis products from cyclohexane and cyanogen-cyclohexane mixtures on both a qualitative and quantitative basis.

Respectfully submitted:

James A. Knight, Jr.
Project Director

Approved:

Richard C. Palmer
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QUARTERLY TECHNICAL STATUS REPORT NO. 6

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
1 OCTOBER 1961 TO 31 DECEMBER 1961
Printed 10 January 1962

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed by
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF ISOTOPE DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During the past quarter major emphasis has been placed on obtaining reproducible G values for the major radiolysis products from irradiated cyclohexane. Gas chromatographic analysis has been utilized. Reproducible G values have been obtained for cyclohexene and dicyclohexyl. Work is currently underway for obtaining G values for the major radiolysis products, including any cyano products, from irradiated mixtures of cyanogen-cyclohexane.

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LIST OF TABLES

This report contains 4 pages.

I. INTRODUCTION

This report summarizes the work performed from October 1, 1961, to December 31, 1961. The purpose of the research work under this contract is the study of radiation-induced cyanogenation, with interest in both the cyano products and the mechanism of the reaction.

Since July, 1, 1961, work on this project has been at a reduced level due to the fact that Mr. Richard Stokes, Research Assistant, is employed for three-fourths time instead of full-time.

A detailed study of the major radiolysis products from irradiated cyclohexane and cyclohexane-cyanogen mixtures is now underway. Particular emphasis is being placed on obtaining quantitative results from which G values can be calculated. During the quarter, 12 irradiations were made of pure cyclohexane and two irradiations were made of mixtures of cyclohexane and cyanogen.

II. EXPERIMENTAL WORK

A. G Values

The experimental procedures for the preparation of samples of cyclohexane and cyanogen-cyclohexane for irradiations and the gas-sampling techniques of the irradiated samples were described in the Quarterly Technical Status Report No. 5.

The G values obtained for the major radiolysis products from some of the irradiations of pure cyclohexane are listed in Table I.

Some irradiations of pure cyclohexane, prior to number 67, are not listed because of the lack of agreement of experimental data. Two mixtures of

TABLE I

G VALUES FROM CYCLOHEXANE

Irradiation Number[a]	Cyclohexane (Grams)	Dose (ev/gm)	G Values[b]		
			Gases[c]	Cyclohexene	Dicyclohexyl
67	9.6	2.9×10^{20}	- -[d]	1.9	- -[e]
68	9.3	2.9×10^{20}	- -	2.0	- -
69	7.8	2.9×10^{20}	- -	2.1	- -
70	8.2	3.1×10^{20}	- -	2.0	2.0
71	7.9	2.3×10^{20}	- -	2.2	2.0
72	8.0	4.9×10^{20}	4.1	1.6	2.1
73	7.9	1.5×10^{21}	4.9	0.95	1.5

[a] All irradiations were performed in the center sample hole of the Cs-137 irradiator.

[b] The dose was determined with the ferrous ion dosimeter and electron density correction applied.

[c] The gases are at least 95 per cent hydrogen.

[d] The gases from irradiations 67 through 71 were not determined.

[e] The dicyclohexyl was not determined for irradiations 67, 68 and 69.

cyclohexane-cyanogen were irradiated and are in the process of being analyzed. The results will be reported in a subsequent report.

B. Gas Chromatographic Analysis

The G values reported in Table I were determined by quantitative gas chromatographic analysis. Cyclohexene was determined with a 12-foot-1/4-inch column, packed with tri-m-cresyl phosphate, 20 per cent by weight, on 30- to 60-mesh Chromosorb P. Dicyclohexyl was determined with a 10-foot-1/4-inch column, packed with Apiezon L, 15 per cent by weight on 50- to 60-mesh acid washed Chromosorb. The gas chromatograph was calibrated for thermal response to cyclohexene and dicyclohexyl under the same conditions as the analyses were performed. Dilute cyclohexane solutions of cyclohexene and dicyclohexyl were used in the calibrations. The areas on the chromagrams were measured with a planimeter.

III. DISCUSSION

Fourteen irradiations were made in the past quarter; twelve of pure cyclohexane and two of cyanogen-cyclohexane mixtures. The irradiated cyclohexane samples were analyzed by gas chromatography for the major radiolysis products: total gases, cyclohexene, and dicyclohexyl. The tentative values found are listed in Table I. The G value of 4.1 for gases (at least 95 per cent hydrogen) from irradiation No. 72 is evidently low as the reported G values for hydrogen from cyclohexane are usually greater than 5. The G value of 4.9 from irradiation No. 73 is much closer to the reported G values. Considerable experimental difficulties have been experienced in the determinations of the radiolytic gases from irradiated cyclohexane. The G value for cyclohexene varies with the dose from 2.2 at a dose of 2.3×10^{20} ev/gm to 0.95 at a dose of 1.5×10^{21} ev/gm. The G value for dicyclohexyl is essentially constant at 2 for dose of 2.3×10^{20} to 4.9×10^{20} ev/gm but decreases to 1.5 at a dose of

1.5×10^{21} ev/gm. The G values given in Table I for cyclohexene and dicyclohexyl from irradiations Nos. 67 through 71 are in reasonable agreement with reported values.

The irradiated mixtures from irradiations Nos. 73 and 74 are being analyzed, and the results will be reported subsequently. The results of the irradiated pure cyclohexane and mixtures of cyanogen-cyclohexane will be compared to determine the effect, if any, of cyanogen on the irradiation.

IV. SUMMARY

Reproducible G values have been obtained for the radiolysis products, cyclohexene and dicyclohexyl, from cyclohexane. The G values for total gases were lower than reported in the literature. Analyses are being made of irradiated cyanogen-cyclohexane mixtures to determine G values for the major radiolysis products, including cyano products.

V. FUTURE PROGRAM

The immediate program will be directed toward a continuation of the gas chromatographic analysis of the major radiolysis products from cyclohexane and cyanogen-cyclohexane mixtures on both a qualitative and quantitative basis.

Respectfully submitted:

James A. Knight, Jr.
Project Director

Approved:

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QUARTERLY TECHNICAL STATUS REPORT NO. 7

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
1 APRIL 1962 TO 30 JUNE 1962

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed by
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During the past quarter, the major emphasis has been on obtaining G values for the major radiolysis products from cyclohexane and mixtures of cyanogen-cyclohexane. G values have been obtained for hydrogen, cyclohexene, and dicyclohexyl from cyclohexane, and it has been found that G values for cyclohexene and dicyclohexyl decrease with increasing dose. G values for cyclohexene, dicyclohexyl, and cyclohexyl cyanide have been obtained from mixtures of cyanogen and cyclohexane. The G values for cyclohexene and dicyclohexyl are less from the mixture than from pure cyclohexane. The G value for cyclohexene from the mixture also decreases with increasing dose, but the G value for dicyclohexyl does not. The G value for cyclohexyl cyanide is about 7 up to a dose of 4.88×10^{20} ev/gm but then decreases to about 5 or less with a dose of 14.6×10^{20} ev/gm. It has also been found that the amount of cyclohexyl cyanide in an irradiated sample decreases with increasing time after irradiation. G values have not been obtained for the components of the gaseous mixture from irradiation cyanogen-cyclohexane mixtures.

TABLE OF CONTENTS

This report contains 10 pages.

I. INTRODUCTION

This report summarizes the work performed from April 1, 1962, to June 30, 1962. The purpose of the research work under this contract is the study of radiation-induced cyanogenation of organic compounds with interest in both the cyano products formed and the mechanism of the reaction.

A detailed study of the major radiolysis products from irradiated cyclohexane and cyclohexane-cyanogen mixtures is now being made. Major emphasis is being placed on obtaining G values for comparison purposes. Cyclohexane was selected for this study for the following reasons.

(a) The radiation chemistry of cyclohexane has been reported in considerable detail in the literature.

(b) There are three reported major radiolysis products from cyclohexane: hydrogen, cyclohexene, and dicyclohexyl.

(c) Cyanogen would yield only one mono cyanide with the parent hydrocarbon, i.e. cyclohexyl cyanide.

II. EXPERIMENTAL WORK

A. Cyanogen

Cyanogen of 99 per cent purity or better is now commercially available and has been used without further purification in the irradiations since November 1961.

B. Preparation of Samples for Irradiation

The procedures for the preparation of samples for irradiation were given in Annual Technical Status Report No. 2.

C. Irradiations and Dosimetry

The center hole of the Cesium-137 Research Irradiator has been utilized since November 1, 1961, for all irradiations. The dose in the center hole as determined with 10 ml of ferrous ion dosimeter solution was found to be 7.77×10^{19} ev/gm/hr.

D. Gas Chromatographic Analysis of Major Radiolysis Products

1. Gaseous Radiolysis Products

The gaseous mixture from irradiations of cyanogen-cyclohexane contain hydrogen, hydrogen cyanide, small quantities of hydrocarbon gases such as methane, and unreacted cyanogen. Several gas chromatographic columns have been tested in an attempt to find one column which would give a satisfactory analysis of the mixture. The columns tested to date include a 5-foot silica gel column, a 5-foot silica gel column coated with 2 per cent di-2-ethylhexyl sebacate, a 12-foot and a 25-foot tri-m-cresyl phosphate column, and a 6-foot Carbowax column. Neither one of the columns tested proved satisfactory for analysis for all of the components of the gaseous mixture. The gaseous mixture can be analyzed by gas chromatography with three different columns as follows: (1) hydrogen, methane, and other hydrocarbon gases on a 5-foot silica gel column; (2) hydrogen cyanide on a 25-foot tetraisobutylene column; and (3) cyanogen on a 12-foot tri-m-cresyl phosphate column.

2. Liquid Radiolysis Products

The gas chromatographic columns used for cyclohexene, dicyclohexyl and cyclohexyl cyanide were listed in Annual Technical Status Report No. 2.

E. G Values

1. G Values for Major Radiolysis Products from Cyclohexane

The G values for the three major radiolysis products from cyclohexane are listed in Table I. The gases were determined volumetrically, and the cyclohexene and dicyclohexyl were determined by gas chromatography.

TABLE I

G VALUES FROM CYCLOHEXANE

G Values[a]		
Gases[b]	Cyclohexene	Dicyclohexyl
4.8 (89)[c]	2.2 (76)	1.5 (76)
4.9 (90)	2.3 (85)	1.5 (85)
---	1.7 (72)	1.3 (72)
5.2 (77)	1.6 (77)	1.3 (77)
4.9 (73)	0.95 (73)	1.0 (73)
---	0.92 (84)	1.0 (84)

Dose (ev/gm)
2.44×10^{20}
2.44×10^{20}
4.88×10^{20}
4.88×10^{20}
14.6×10^{20}
14.6×10^{20}

[a] The dose was determined with the ferrous ion dosimeter and electron density correction applied.

[b] The gases are reported to be at least 95 per cent hydrogen.

[c] The numbers in parentheses are the irradiation numbers.

2. G Values for Major Radiolysis Products from Cyanogen-Cyclohexane Mixtures

G values for the major liquid radiolysis products from mixtures of cyanogen-cyclohexane have been determined by gas chromatography and are listed in Table II. To date, hydrogen and hydrogen cyanide have been identified in the radiolytic gaseous mixture. Also, cyanogen is present in both the radiolytic gaseous mixture and the irradiated liquid, including those samples which were irradiated for a total dose of 1.46×10^{21} ev/gm.

TABLE II

G VALUES FROM CYANOGEN-CYCLOHEXANE MIXTURES

G values			
Cyclohexene	Dicyclohexyl	Cyclohexyl Cyanide	Dose (ev/gm)
0.99 (82)[a]	0.35 (82)	6.6 (91)	2.44×10^{20}
1.2 (86)	0.34 (86)	7.5 (86)	2.44×10^{20}
0.72 (81)	0.36 (81)	7.6 (93)	4.88×10^{20}
0.82 (88)	0.36 (88)	6.9 (88)	4.88×10^{20}
0.56 (79)	0.41 (79)	5.0 (94)	14.6×10^{20}
0.51 (80)	0.44 (80)	4.2 (95)	14.6×10^{20}

[a]The numbers in parentheses are the irradiation numbers.

F. Cyclohexyl Cyanide

1. Decrease in Yield of Cyclohexyl Cyanide With Time

In rechecking some of the G values for cyclohexyl cyanide, it was found that the amount of cyclohexyl cyanide in the irradiated sample decreased with increasing time after irradiation. Therefore, two irradiations were made and analyzed for cyclohexyl cyanide as soon as possible after removal from the source and at varying intervals over a period of 35 days. It was found that the amount of cyclohexyl cyanide decreased with increasing time after irradiation. The data are given in Table III, and the decrease is shown in terms of G values.

TABLE III

DECREASE IN CYCLOHEXYL CYANIDE
WITH TIME AFTER IRRADIATION

Time After Irradiation (Days)	G Values, Cyclohexyl Cyanide	
	Irradiation No. 86 (Dose-2.44 x 10^{20} ev/gm	Irradiation No. 88 (Dose-4.88 x 10^{20} ev/gm
1	7.5	6.9
3	6.8	---
10	4.5	4.2
24	2.3	2.3
29	2.1	2.0
35	1.7	1.7

2. Distillation of an Irradiated Sample

A 5 ml sample of irradiation no. 93, dose 4.88×10^{20} ev/gm, was vacuum distilled at about 2 mm pressure and 50° C. All of the sample did not distill at these conditions. Cyclohexyl cyanide would distill at these conditions as it has a boiling point of 72°-73° C at 16 mm pressure. The distillate, which contained cyclohexyl cyanide as determined by gas chromatography, and the irradiated liquid were analyzed for cyclohexyl cyanide at varying times intervals. The results are summarized in Table IV, with the amount of cyclohexyl cyanide expressed in G values.

TABLE IV

G VALUES FOR CYCLOHEXYL CYANIDE FOR
NONDISTILLED AND DISTILLED SAMPLES FROM IRRADIATION NO. 93

Time After Irradiation (Days)	G Values, Cyclohexyl Cyanide	
	Nondistilled	Distilled
1	7.6	2.2
2	6.4	2.5
12	5.1	2.6
35	3.8	2.6

From this experiment, it is evident that the amount of cyclohexyl cyanide in the nondistilled sample decreases with time as shown above for irradiations nos. 86 and 88, that the amount of cyclohexyl cyanide distilling is about one-third of that present, and that the cyclohexyl cyanide in the distilled material does not decrease with time.

3. Evidence for Cyclohexyl Cyanide

The evidence for cyclohexyl cyanide has been obtained from infrared spectroscopy and gas chromatography. An irradiated sample was distilled slowly at atmospheric pressure to remove most of the cyclohexane, thus concentrating the cyclohexyl cyanide. The infrared spectra of this concentrated product showed absorption at 4.4 microns which is attributed to the cyano group, $-C \equiv N$, and it also compared favorably with the spectra of a sample of authentic cyclohexyl cyanide.

The cyclohexyl cyanide has been identified on two different gas chromatographic columns, an Apiezon L column and an Ucon oil LB-550-X. Identification has been by comparison of retention times and by enrichment of irradiated samples with cyclohexyl cyanide.

G. Preparation of Cyclohexyl Cyanide[1]

Cyclohexanecarboxylic acid, 66 gm, and 61 ml of thionyl chloride were refluxed on a steam bath for an hour. The reaction mixture was added to 600 ml of conc. ammonium hydroxide cooled to 5° C. The temperature was not allowed to rise above 10° C during the addition. The solid amide was removed, washed with several portions of water and dried. The melting point of the amide was 185° C (uncorr.); reported, 185°-6° C; yield, 37 gm.

The amide was refluxed overnight with 61 ml of thionyl chloride to convert it to the cyanide. The crude cyclohexyl cyanide was fractionally distilled at 19 mm; b. pt. 77°-78° C; $n_D^{20°}$ 1.4534. Reported values:[2] b. pt. 72°-73° C at 16 mm; n_D^{19} 1.4543.

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[1] D. S. Breslow and C. R. Hauser, J. Am. Chem. Soc., 67, 686 (1945).

[2] C. A. 45: 1077 i.

III. DISCUSSION

Reproducible G values for the three major radiolysis products, hydrogen, cyclohexene and dicyclohexyl, have been obtained from cyclohexane with doses varying from 2.44×10^{20} to 14.6×10^{20} ev/gm. The G values for hydrogen do not show any variation with dose and are slightly less than most reported values, which are in the range of 5.2 to 5.5. The G values for both cyclohexene and dicyclohexyl show a decrease with increasing dose. This decrease is at variance with some of the reported work. The values of G (cyclohexene) = 2.2 and G (dicyclohexyl) = 1.5 at 2.44×10^{20} ev/gm are in agreement with the values reported by Nevitt and Remsberg.[3]

The gaseous mixture from irradiations of cyanogen-cyclohexane contains hydrogen, hydrogen cyanide, small quantities of hydrocarbon gases such as methane, and unreacted cyanogen. To date, no one gas chromatographic column has been found which will give a satisfactory analysis of the mixture. The mixture can be analyzed by gas chromatography with three different columns as follows: (1) hydrogen, methane, and other hydrocarbon gases on a silica gel column; (2) hydrogen cyanide on a 25-foot tetraisobutylene column; and (3) cyanogen on a 12-foot tri-m-cresyl phosphate column. To date, satisfactory quantitative analyses of the radiolytic gaseous mixtures have not been obtained. Additional work is planned on this phase of the program.

The G values for cyclohexene from the mixtures are less than from pure cyclohexane and also show a decrease with increasing dose. The G values for dicyclohexyl from the mixtures are considerably less than from pure cyclohexane, but do not show any great variation with increasing dose.

The G values for cyclohexyl cyanide, obtained by analyzing the mixtures

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[3] T. D. Nevitt and L. P. Remsberg, J. Phys. Chem., 64, 969 (1960).

as soon as possible after irradiation, are about 7 for 2.44 - 4.88 x 10^{20} ev/gm, but then decrease to 5 or less with an increase in dose to 14.6 x 10^{20} ev/gm. The reason for the decrease in the yield of cyclohexyl cyanide with increasing dose is not evident. It could be due to the fact that the amount of cyanogen is decreasing with increasing dose, or that the cyclohexyl cyanide is undergoing some radiolytic reaction, or a combination of these things. It has also been found that the amount of cyclohexyl cyanide in the irradiated sample decreases with increasing time. Table III gives the decrease in terms of G values up to a period of 35 days after irradiation. The reason for the decrease of cyclohexyl cyanide in the mixture with increasing time after irradiation is not evident. A sample of a mixture was distilled shortly after irradiation at 1-2 mm and 50° C to separate the material volatile at these conditions from any nonvolatile material. The cyclohexyl cyanide, which boils at 72°-73° C at 16 mm, should be in the distillate. Analyses of the distillate showed that 30-35% of the cyclohexyl cyanide had distilled. Analyses of this distillate has shown that the amount of cyclohexyl cyanide does not decrease with time. This indicates that the disappearance is due to some material contained in the irradiated sample which is not volatile. Additional work is planned on this particular aspect of the problem.

IV. SUMMARY

Reproducible G values have been obtained for hydrogen, cyclohexene, and dicyclohexyl from cyclohexane. The G values for both cyclohexene and dicyclohexyl decrease with increasing dose. Reproducible G values for cyclohexene, dicyclohexyl and cyclohexyl cyanide have been obtained from mixtures of cyanogen and cyclohexane. The G values for cyclohexene and dicyclohexyl are less from the mixture than from pure cyclohexane. The G values for cyclohexene from the

mixture also decrease with increasing dose, but the G value for dicyclohexyl does not. The G value for cyclohexyl cyanide is about 7 up to a dose of 4.88 x 10^{20} ev/gm but then decreases to about 5 or less with a dose of 14.6 x 10^{20} ev/gm. It has also been found that the amount of cyclohexyl cyanide in an irradiated sample decreases with increasing time. G values have not been obtained for the components of the gaseous mixture from irradiated cyanogen-cyclohexane mixtures. A system of analysis for the major components by gas chromatography has been worked out.

V. FUTURE PROGRAM

The immediate program will be directed toward: (1) additional work on the problem of the decrease in the amount of cyclohexyl cyanide in an irradiated sample; (2) additional work on the analysis of the gaseous mixture from the irradiated cyanogen-cyclohexane mixtures; and (3) additional irradiations of mixtures containing cyanogen.

Respectfully submitted:

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Project Director

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY TECHNICAL STATUS REPORT NO. 8

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
1 JULY 1962 TO 30 SEPTEMBER 1962

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed by
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

During the past quarter, the major emphasis has been on the determination of radiolytic gases from irradiated cyanogen-cyclohexane mixtures and on the problem of the decrease in the amount of cyclohexyl cyanide in an irradiated mixture with increasing time after irradiation. The major radiolytic gases are hydrogen, $G \sim 3.4$, and hydrogen cyanide, $G \sim 2.4$, for dose of 2.44×10^{20} ev/gm. It has been found that treatment of the irradiated mixture with either 5 per cent potassium hydroxide solution or potassium hydroxide pellets immediately after irradiation prevents a decrease in the amount of cyclohexyl cyanide. Also, the G values for cyclohexyl cyanide for the base-treated irradiated mixtures are in the range of 18 to 20 for mixtures irradiated to a dose of 2.44×10^{20} ev/gm.

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This report contains 8 pages.

LIST OF TABLES

I. INTRODUCTION

The report summarizes the work performed from July 1, 1962, to September 30, 1962. The purpose of the research work under this contract is the study of radiation-induced cyanogenation of organic compounds with interest in both the cyano products formed and the mechanism of the reaction.

During the past quarter attention has been given to the determination of radiolytic gases from irradiated cyanogen-cyclohexane mixtures and to the problem of the decrease in the amount of cyclohexyl cyanide in an irradiated mixture with increasing time after irradiation.

Mr. Richard Stokes, research assistant on this project, resigned in the early part of September to continue his education at another institution. Due to this fact, the work has been at a reduced level since that time. Since the project is not to be renewed, it will not be feasible to replace him.

II. EXPERIMENTAL

A. Irradiations

The procedures for the preparation of samples for irradiation have been given in previous reports. The center hole of the Cesium-137 Research Irradiator is currently employed for irradiations.

B. Gas Chromatographic Analysis

1. Gaseous Mixture from Irradiations

The gaseous mixture from an irradiation of cyanogen-cyclohexane contains the radiolytic products--hydrogen and hydrogen cyanide--in addition to cyclohexane vapor and unreacted cyanogen. Under the conditions of gas

chromatographic analysis employed, hydrocarbon gases, such as methane, have not been detected. The total volume of the gas mixture from an irradiation is determined and then samples are analyzed for hydrogen and cyanogen by gas chromatographic techniques. The hydrogen is analyzed with a 5-foot silica gel column, and the cyanogen is analyzed with a 12-foot tri-m-cresyl phosphate column. The hydrogen cyanide is determined by difference, taking into account the presence of cyclohexane vapor.

The G values for hydrogen and hydrogen cyanide are given in Table I.

TABLE I

G VALUES FOR HYDROGEN AND HYDROGEN CYANIDE

	G Values	
Product	Irradiation No. 99[a]	Irradiation No. 101
Hydrogen	3.7	2.8
Hydrogen Cyanide	2.2	2.5

[a]Dose for each irradiation--2.44×10^{20} ev/gm.

The cyanogen remaining after irradiation was determined in both the gaseous and liquid phases, and the results are given in Table II.

TABLE II

CYANOGEN REMAINING AFTER IRRADIATION

Irradiation No.	Total Cyanogen Remaining (ml, STP)	Total Cyanogen in Original Sample (ml, STP)	Cyanogen Consumed (%)
99	32	90	64.5
101	26	89	71.8

2. Cyclohexyl Cyanide

Cyclohexyl cyanide is determined with a 9-foot Ucon Oil LB-550X column. The gas chromatographic unit was calibrated for thermal response to cyclohexyl cyanide with dilute solutions of cyclohexyl cyanide in cyclohexane.

C. Treatment of Irradiated Mixtures

From previous work, it had been determined that the amount of cyclohexyl cyanide in an irradiated mixture decreased with time after irradiation. (See Table III, Quarterly Technical Status Report No. 7, Project No. A-446-8.) Samples of irradiated cyanogen-cyclohexane were treated immediately after irradiation by the methods given below and were then analyzed by gas chromatography for cyclohexyl cyanide at varying time intervals.

a. Approximately 2 ml of the irradiated mixture was washed with an equal volume of 5 per cent potassium hydroxide solution, washed free of base, and dried with anhydrous magnesium sulfate.

b. Approximately 2 ml of the irradiated mixture was washed with an equal volume of 5 per cent hydrochloric acid, washed free of acid, and dried with anhydrous magnesium sulfate.

c. Approximately 2 ml of the irradiated mixture was washed with an equal

volume of 5 per cent hydroxide followed by a wash with an equal volume of 5 per cent HCl. The mixture was washed free of acid and dried with anhydrous magnesium sulfate.

d. Approximately 2 ml of the irradiated mixture was washed with an equal volume of water and dried with anhydrous magnesium sulfate.

e. Two potassium hydroxide pellets were added to approximately 2 ml of the irradiated mixture.

f. A small sample of the irradiated mixture was retained without any treatment.

Qualitatively, the treatments gave the following results.

Treatment a - The amount of cyclohexyl cyanide was greater after washing with 5 per cent potassium hydroxide.

Treatment b - The amount of cyclohexyl cyanide was essentially zero after washing with 5 per cent hydrochloric acid.

Treatment c - The amount of cyclohexyl cyanide was essentially the same as obtained by washing with 5 per cent potassium hydroxide alone, and was unaffected by the subsequent 5 per cent hydrochloric acid wash.

Treatment d - The amount of cyclohexyl cyanide was not affected by the water wash.

Treatment e - The amount of cyclohexyl cyanide in an irradiated sample containing potassium hydroxide pellets showed an initial increase upon standing and then reached an essentially constant value.

The quantitative results, expressed as G values, are given in Tables III and IV.

TABLE III

CYCLOHEXYL CYANIDE FROM IRRADIATION NO. 99

Time After Irradiation (Days)	G Values for Cyclohexyl Cyanide[a]			
	Original Mixture	5% KOH	KOH Pellets	5% KOH and 5% HCl
1	3.9	18.3	9.1	18.4
6	3.6	16.4	19.3	15.1
22	3.0	17.0	20.4	16.0

[a]Dose--2.44 x 10^{20} ev/gm.

TABLE IV

CYCLOHEXYL CYANIDE FROM IRRADIATION NO. 101

Time After Irradiation (Days)	G Values for Cyclohexyl Cyanide[a]	
	5% KOH	KOH Pellets
1	14.0	7.0
7	15.4	19.1
22	13.3	19.3
35	17.2	20.6

[a]Dose--2.44 x 10^{20} ev/gm.

III. DISCUSSION

The G values for hydrogen from the irradiated mixtures, although not in good agreement, are less than the G values for hydrogen from irradiated cyclohexane. The G values for hydrogen cyanide are in fair agreement for the two irradiations. These values indicate that a portion of the hydrogen is formed by a process which the cyanogen affects, and that the formation of hydrogen cyanide must be considered in the radiation chemistry of the cyclohexane-cyanogen system.

The amounts of cyanogen consumed in the two irradiations are in fair agreement. In order to form hydrogen cyanide with a G = 2.5 and cyclohexyl cyanide with a G = 20 (as determined by KOH pellet treatment), approximately 8 ml (STP) of cyanogen would be required. Of the 63 ml of cyanogen comsumed in irradiation No. 101, 55 ml were used by some process other than the formation of hydrogen cyanide and cyclohexyl cyanide. No other organic cyanides have been identified. Some cyanogen is most likely consumed in the formation of a brownish insoluble material which has been present in the irradiated mixtures.

The cyclohexyl cyanide produced in the irradiation presents a complex problem. First of all, there is the decrease of cyclohexyl cyanide with increasing time after irradiation as shown in Table III, Quarterly Technical Status Report No. 7. The G values for cyclohexyl cyanide from irradiation No. 99 are not in good agreement with those of irradiations Nos. 86 and 88.

From the treatment of samples of the irradiated mixtures with either 5 per cent potassium hydroxide or potassium hydroxide pellets, there is an increase in the amount of cyclohexyl cyanide. The agreement for these two modes of treatment from irradiations Nos. 99 and 101 is fairly good. Evidently a good part of the cyclohexyl cyanide present in the irradiated mixture is

bound in a "complex form" that is destroyed by the base.

The washing of samples of the irradiated mixture with 5 per cent hydrochloric acid must catalyze the process by which the cyclohexyl cyanide is removed. The effect of 5 per cent hydrochloric acid is not due to the removal of the cyclohexyl cyanide by the hydrochloric acid. Known solutions of cyclohexyl cyanide in cyclohexane were washed with 5 per cent hydrochloric acid in the same manner as the irradiated mixture. The original and washed solutions were analyzed for cyclohexyl cyanide by gas chromatography, and the results showed the same amount of cyclohexyl cyanide after washing as for the original solution. This is also supported by the fact that the washing of an irradiated sample with 5 per cent potassium hydroxide solution followed by washing with 5 per cent hydrochloric acid solution gives a sample in which the amount of cyclohexyl cyanide is essentially the same as for an irradiated sample washed only with 5 per cent potassium hydroxide solution.

IV. SUMMARY

The yield of hydrogen is less from the irradiated cyanogen-cyclohexane mixtures than from irradiated pure cyclohexane. Hydrogen cyanide is formed in the irradiation of the mixtures. The cyclohexyl cyanide produced presents a complex problem. The cyclohexyl cyanide appears to be removed from the irradiated mixture through the formation of a "complex product." The treatment of an irradiated mixture immediately after irradiation with potassium hydroxide evidently destroys and prevents the "complex product" formation. Hydrochloric acid appears to act as a catalyst for the "complex product" formation.

V. FUTURE PROGRAM

The remaining time on the project will be spent on performing a few additional irradiations and on preparation of the final report.

Respectfully submitted:

James A. Knight, Jr.
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

December 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Quarterly Technical Status Report No. 9, Project No. A-446-8
"Radiation-Induced Cyanogenation of Organic Compounds"
Contract No. AT (38-1)-202, Task No. VIII
Covering the Period from October 1 to December 31, 1962

Gentlemen:

A quarterly technical status report will not be prepared for the above period as the final report is being prepared and will be submitted for approval when completed.

During the past quarter, the work has been at a reduced level. Attention was given to completing portions of the laboratory work and preparation of the final report.

During the coming month, attention will be given to completing the final report.

Respectfully submitted,

James A. Knight, Jr.
Project Director

ANNUAL TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

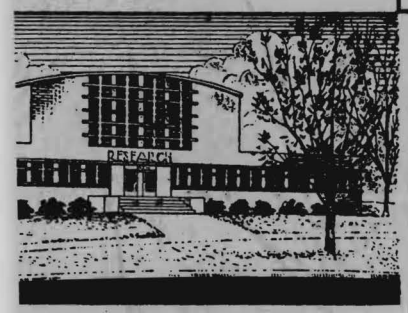
By

JAMES A. KNIGHT, JR. AND COLEMAN J. BRYAN

COVERING THE PERIOD
1 MAY 1960 TO 31 MARCH 1961
Printed 20 April 1961

CONTRACT NO. AT (38-1)-202
TASK NO. VIII
Placed By
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

LEGAL NOTICE

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

ANNUAL TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-8

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ABSTRACT

The overall broad objectives of this research program are to study the effects of ionizing radiation on the cyanogenation of organic compounds. During the period covered by this report, emphasis was placed on: (1) the irradiation of cyanogen-organic mixtures; and (2) the analysis of the irradiated mixtures for cyano products and for unconsumed cyanogen. The organic compounds that have been irradiated in admixture with cyanogen are benzene, toluene, n-heptane, cyclohexane, 2,4,4-trimethylpentene-1, 2,2,4-trimethylpentane, 2-methylpentane, and 3-methylhexane. Infrared analysis of the irradiated mixtures indicated that radiation-induced cyanogenation occurred with all of the above organic compounds. In two experiments at room temperature in the absence of ionizing radiation, cyanogenation did not occur.

Irradiations have been conducted in both sealed glass irradiation tubes and a stainless steel bomb. The utilization of a stainless steel bomb permits a much higher ratio of cyanogen to organic compound to be employed than with the glass irradiation tubes.

All irradiations to date have been carried out on a relatively small scale in the 12-kilocurie Cesium-137 Research Irradiator. Dosimetry determinations, employing the same geometry and similar irradiation tubes, have been made with the ferrous ion dosimeter.

An acceptable quantitative method has been developed for the determination of cyanogen dissolved in an organic compound. The solubilities of cyanogen have been determined in each of the hydrocarbons used to date in the irradiations.

A gas chromatographic unit was obtained, and studies of column packings that will be suitable for analysis of cyanogen and the radiolysis products are currently underway.

TABLE OF CONTENTS

This report contains 26 pages.

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

This report summarizes the work performed during the 11 months from May 1, 1960, to March 31, 1961 and is submitted as the first annual report. The purpose of the research under this contract is to study radiation-induced cyanogenation of organic compounds, with interest not only in the products of the reactions, but also in the mechanism of the reactions.

During the period covered by this report, a total of 44 irradiations were made as follows: (a) 35 on mixtures of cyanogen-organic compounds; (b) 8 on pure organic compounds; and (c) 1 on pure cyanogen. Infrared spectra were obtained on the distillates and flask residues of the irradiated mixtures, and the differences in the spectra of the samples from the irradiated cyanogen-organic mixtures and the irradiated pure organic compounds were examined. Infrared spectra indicated that radiation-induced cyanogenation occurred with all hydrocarbons used in admixture with cyanogen.

Two blank runs, cyanogen--n-heptane and cyanogen--2,4,4-trimethylpentene-1, were made in the absence of high energy radiation; the cyanogen-hydrocarbon mixtures were sealed in reaction tubes and allowed to stand at room temperature for 168 hours. No reaction occurred.

The solubility of cyanogen in benzene, toluene, cyclohexane, n-heptane, 2,2,4-trimethylpentane, and 2,4,4-trimethylpentene-1 at 25.0° C has been determined.

II. EXPERIMENTAL WORK

A. Preparation and Handling of Cyanogen

After examination of various methods for the synthesis of cyanogen, the

method employed by Janz[1] was selected as being the most suitable. This method consists of treating dry copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) with an excess of a saturated solution of sodium cyanide. The preparation is carried out in an all-glass apparatus in a well-ventilated hood. The rate of evolution of cyanogen is controlled by carefully regulating the addition of the saturated solution of sodium cyanide. During the preparation of cyanogen, the apparatus is continuously swept with nitrogen. The gases are bubbled through silver nitrate solution to remove any hydrogen cyanide and then passed through two drying towers of phosphorous pentoxide supported on glass wool. The cyanogen is condensed in a cold trap in a dry ice-acetone bath. The exhaust gases from the cold trap bubble through a potassium hydroxide solution which removes any remaining cyanogen. The yields of approximately 40 per cent agree with those reported by Janz.

B. Quantitative Determination of Cyanogen

It has been reported that cyanogen reacts quantitatively with sodium hydroxide or potassium hydroxide solutions to yield the alkali cyanide and cyanate.[2] This reaction forms the basis of the method for the quantitative determination of cyanogen. The cyanogen is reacted with an excess of 1M potassium hydroxide solution and the potassium cyanide formed is then titrated with standard silver nitrate solution to the first permanent turbidity. The addition of

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[1] G. Janz, Inorganic Synthesis, edited by T. Moeller, McGraw-Hill Co., Inc., New York, N. Y. (1957), Vol. V., p. 43.

[2] F. H. Rhodes, J. Ind. and Eng. Chem. 4, 652 (1912).

a small quantity of potassium iodide gives a sharper end-point.

C. Transferring Cyanogen

The preferred method for transferring cyanogen is distillation by use of cold traps in an all-glass apparatus. This method is time-consuming as approximately 3 hours are required to transfer 0.5 gm. The method now being employed is one of direct transfer with a spatula cooled to dry ice-acetone temperature. This method has proven satisfactory and is very time-saving.

D. Irradiation Tubes and Holders

An irradiation tube and a brass irradiation tube-holder were designed and fabricated for the outside holes of the Cesium-137 Research Irradiator[3] (Figure 1). The reaction tube is glass and of sufficient size to allow for possible vaporization of cyanogen during irradiation. During an irradiation the tube is sealed. The cap of the brass tube-holder has an exhaust tube so that the brass tube-holder is evacuated continuously during an irradiation. Should the glass irradiation tube break, the exhaust tube will prevent the release of any gaseous substances into the laboratory. The brass tube-holder would also prevent spilling of any liquid resulting from breakage of the glass irradiation tube. One end of a 15-foot section of airplane cable for raising and lowering the brass tube-holder is soldered into the cap. In addition, the brass tube-holder contains a thermocouple so that the temperature can be monitored during an irradiation.

A stainless steel bomb--30-ml. capacity, 1-inch-outside-diameter and 4-

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[3] R. C. Palmer and R. W. Carter, Int. J. App. Rad. and Isotopes 9, 123 (1960).

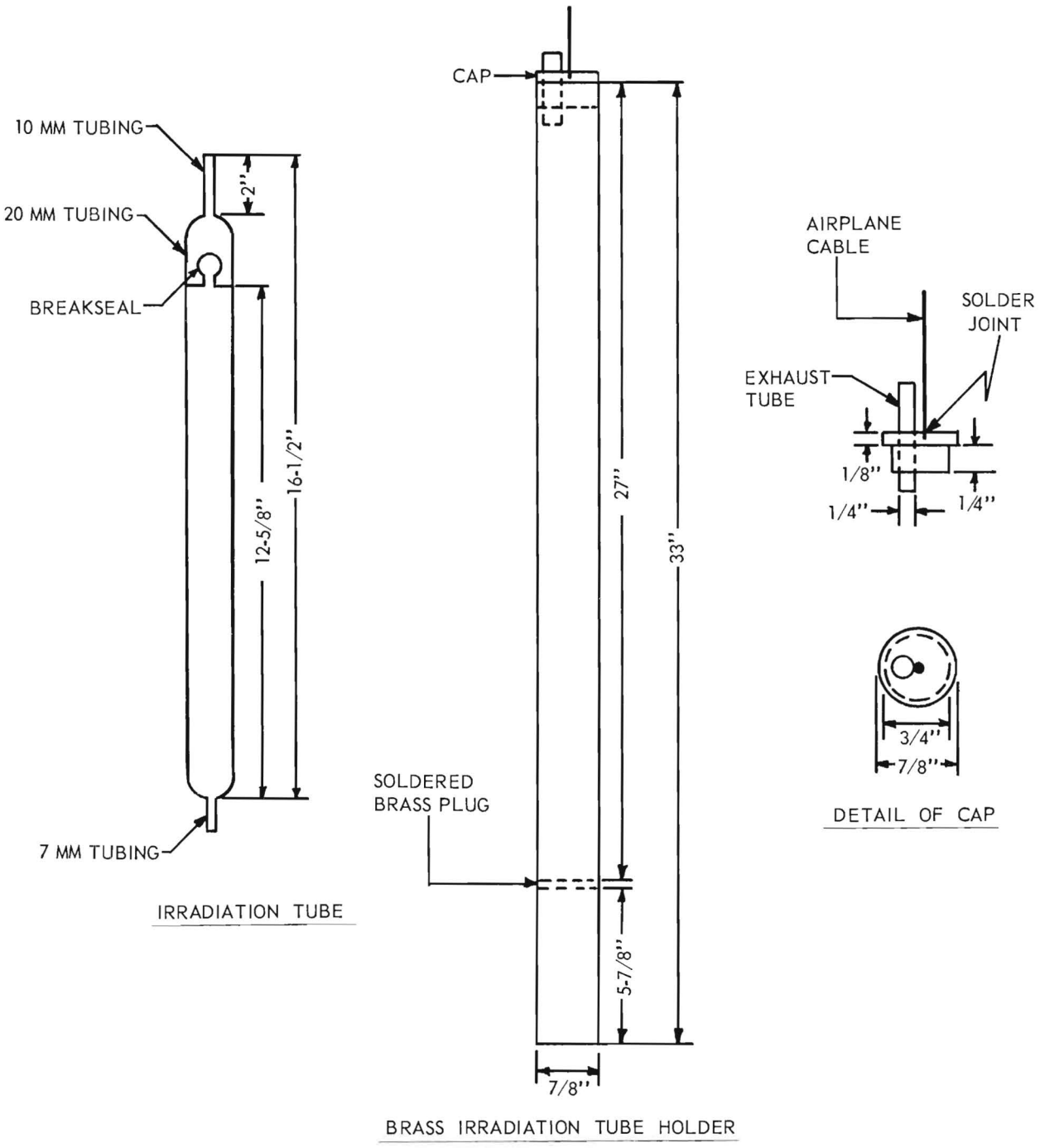

Figure 1. Irradiation Tube and Holder for the Outer Sample Holes of the Cesium-137 Research Irradiator.

inch-length was obtained so that larger ratios of cyanogen to organic compound could be employed than possible with the glass irradiation tube. A similar brass tube was fabricated to hold this stainless steel bomb in the center hole of the irradiator. The cap of the brass holder has an exhaust tube for continuous evacuation during irradiation. A 15-foot section of airplane cable for raising and lowering the holder is soldered into the cap. Provision is also made for a thermocouple in order to monitor the temperature during irradiation.

E. Dosimetry Determinations

Dosimetry determinations were made in a glass reaction tube encased in a brass irradiation tube holder so marked that the tube holder for each sample hole may be readily identified and used only in that sample hole. The ferrous ion dosimeter was employed. Measurements in outside sample hole No. 1 showed a dose of $(7.59 \pm 0.12) \times 10^5$ rad/hr, No. 11, a dose of $(7.62 \pm 0.15) \times 10^5$ rad/hr, and No. 12, a dose of $(8.89 \pm 0.09) \times 10^5$ rad/hr.

Additional dosimetry determinations were made on the center hole of the irradiator. This study was made in a stainless steel bomb encased in a brass holder. Measurement in the center hole with this experimental setup gave a dose of $(1.01 \pm 0.01) \times 10^6$ rad/hr.

F. Irradiation of Cyanogen-Organic Mixtures

The cyanogen-organic mixtures for irradiation in the glass tubes were prepared by weighing the reaction tube, introducing a known amount of the organic compound into the glass reaction tube at dry ice-acetone bath temperatures, adding the cyanogen to the organic compound, sealing the reaction tube, and again weighing the reaction tube after the contents reached room temperature. The weight of cyanogen added was then determined. The reaction tube was placed in

a brass irradiation tube holder fitted with an exhaust tube and thermocouple, and the whole assembly placed in the irradiator.

A stainless steel bomb was obtained so that mixtures with larger ratios of cyanogen to organic compounds could be irradiated. One irradiation with a molar ratio of cyanogen to benzene of one to three was carried out as follows: The bomb was charged by generating cyanogen directly into the bomb, carefully adding a known weight of benzene at dry ice-acetone temperature and then sealing with a brass valve. The bomb was weighed at room temperature, sealed in a brass holder fitted with an exhaust valve and thermocouple, and placed in the irradiator.

The irradiated contents of the glass irradiation tubes and bomb were treated as follows: The amount of cyanogen remaining after irradiation was determined by extraction and titration as described in B above. The organic phase was then dried with magnesium sulfate, filtered, and distilled. Infrared spectra were obtained on both the flask residue and the distillate, and the spectra were examined for nitrile and amine absorption bands.

The organic compounds investigated thus far in admixture with cyanogen are benzene, toluene, cyclohexane, n-heptane, 2,2,4-trimethylpentane, 2-methylpentane, 3-methylhexane, and 2,4,4-trimethylpentene-1. Infrared absorption at 4.4 microns, which is attributed to the nitrile radical, has been observed for the flask residues for all of the above organic compounds. In addition to the nitrile absorption at 4.4 microns, the infrared spectra of the flask residues of irradiations Nos. 10, 11, 12, and 15 showed absorption at 2.92 which could be attributed to the presence of an amine grouping.

The results of the cyanogen-organic mixtures , except Nos. 29 through 34, are summarized in Table I and the comments on the infrared spectra are given in

Table II.

TABLE I

IRRADIATIONS OF CYANOGEN-ORGANIC MIXTURES

Irradiation Mixture Number[a]	Organic Compound (Moles)	Cyanogen (Moles)	Period of Irradiation (Hours)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
1	Benzene 0.11	0.0052	3	0.0022	0.0030	1.6×10^{20}
3	Benzene 0.11	0.0097	8	0.0041	0.0056	4.2×10^{20}
4	Benzene 0.11	0.0102	7	0.0052	0.0050	3.6×10^{20}
6	Benzene 0.255	0.0174	18	-----[b]	-----	9.5×10^{20}
7	Toluene 0.246	0.0352	24	0.0067	0.0285	1.3×10^{21}
8	n-Heptane 0.171	0.0308	72	0.0115	0.0193	3.8×10^{21}
9	Benzene 0.275	0.0242	163	0.0202	0.0040	8.6×10^{21}
10	n-Heptane 0.171	0.0065	168	0.0030	0.0035	8.9×10^{21}
11	Toluene 0.235	0.0119	168	0.0027	0.0092	7.7×10^{21}
12	Cyclohexane 0.232	0.0116	168	0.0003	0.0113	8.9×10^{21}
15	2,2,4-Trimethylpentane 0.152	0.0164	168	0.0132	0.0032	8.9×10^{21}
19	2,4,4-Trimethylpentene-1 0.150	0.0306	168	0.0227	0.0079	8.9×10^{21}

(Continued)

TABLE I (Continued)

IRRADIATIONS OF CYANOGEN-ORGANIC MIXTURES

Irradiation Mixture Number[a]	Organic Compound (Moles)	Cyanogen (Moles)	Period of Irradiation (Hours)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Dose (ev/gm)
21	2-Methylpentane 0.206	0.0220	168	0.0127	0.0093	8.9×10^{21}
22	3-Methylhexane 0.172	0.0298	168	0.0200	0.0098	7.7×10^{21}
23	Benzene 0.225	0.0078	168	0.0006	0.0072	1.0×10^{22}
24	Cyclohexane 0.232	0.0167	168	0.0057	0.0110	8.9×10^{21}
25	Cyclohexane 0.232	0.0147	168	0.0035	0.0112	7.7×10^{21}
26	Cyclohexane 0.232	0.0297	168	0.0056	0.0240	8.9×10^{21}
27	Cyclohexane 0.232	0.0045	168	0.0004	0.0041	7.7×10^{21}
28	Benzene 0.225	0.0784	168	0.0404	0.0380	1.0×10^{22}
35	Benzene 0.225	0.0414	311.5	-----[c]	-----	1.9×10^{22}

[a] All irradiations except Nos. 28 and 35 were performed in glass irradiation tubes. Irradiation Nos. 28 and 35 were performed in a stainless steel bomb.

[b] It was not possible to titrate this sample due to the black color of the potassium hydroxide.

[c] It was not possible to measure the amount of cyanogen remaining as a leak developed upon measurement of the pressure in the bomb after irradiation.

TABLE II

COMMENTS ON INFRARED SPECTRA

Irradiation No.	Distillate	Residue in Flask
1	Very similar to pure benzene	Identical with flask residue of irradiated benzene
3	Very similar to pure benzene	Identical with flask residue of irradiated benzene
4	Very similar to pure benzene	Identical with flask residue of irradiated benzene
5	Identical to pure benzene	Identical with flask residue of irradiated benzene
7	Very similar to pure toluene	No nitrile peak observed.
8	Identical to pure n-heptane	Possible nitrile peak at 4.4 microns
9	Identical to pure benzene	Identical with flask residue of irradiated benzene
10	Very similar to pure n-heptane	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns
11	Very similar to pure toluene	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns
12	Very similar to pure cyclohexane	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns
15	Very similar to pure 2,2,4-trimethylpentane	Possible nitrile peak at 4.4 microns and amine peak at 2.92 microns

(Continued)

TABLE II (Continued)

COMMENTS ON INFRARED SPECTRA

Irradiation No.	Distillate	Residue in Flask
19	Identical to pure 2,4,4-trimethylpentene-1	Possible nitrile peak at 4.4 microns
21	Very similar to pure 2-methylpentane	Possible nitrile peak at 4.4 microns
22	Very similar to pure 3-methylhexane	Possible nitrile peak at 4.4 microns
23	Identical to pure benzene	No nitrile peak observed
24	Very similar to pure cyclohexane	Possible nitrile peak at 4.4 microns
25-27[a]	Very strong peak at 4.4 microns upon second distillation	No observable nitrile peak after second distillation
28	Identical to pure benzene	Possible nitrile peak at 4.4 microns
35	Not run	Possible nitrile peak at 4.4 microns equal in intensity to the C-H peak at 3.2 microns

[a]The residues from the first distillation of these three irradiations were combined and distilled at 260° C and 2 mm pressure. The distillate was a clear yellow material and contained 4.66 per cent nitrogen.

Several cyanogen-cyclohexane mixtures were irradiated with a constant weight of cyclohexane and varying amounts of cyanogen. The results are shown in Table III. The flask residues from the first distillations of these irradiations were combined and redistilled from a special apparatus at 260° C and 2 mm pressure. The distillate, 0.3275 gm, showed a strong nitrile peak at 4.40 microns while the flask residue gave no peak.

TABLE III

IRRADIATIONS OF CYANOGEN-CYCLOHEXANE MIXTURES

Irradiation Mixture No.[a]	Period of Irradiation (Hours)	Cyanogen (Moles)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)	Cyanogen Consumed (%)	Dose (ev/gm)
32	24	0.0072	0.0060	0.0012	16.6	1.1×10^{21}
29	48	0.0092	0.0058	0.0034	37.0	2.2×10^{21}
30	72	0.0085	0.0045	0.0040	47.0	3.8×10^{21}
31	96	0.0169	0.0124	0.0045	26.6	4.4×10^{21}
34	120	0.0078	0.0030	0.0048	61.5	6.4×10^{21}
33	144	0.0089	0.0026	0.0063	71.0	6.6×10^{21}

[a] In each irradiation, 0.232 mole of cyclohexane was used.

G. Blank Experiments

Two mixtures, cyanogen--n-heptane and cyanogen--2,4,4-trimethylpentene-1, were prepared in the same manner as for irradiation. These mixtures, after standing at room temperature for 168 hours, were treated in the same manner as an irradiated mixture. The cyanogen remaining indicates that no reaction took

place in either case (Table IV). Gas chromatographic analysis of the organic phase from each experiment showed only the pure compound present. Infrared curves of the organic phase did not show any absorption that could be attributed to the cyano group. These results show that no cyanogenation occurred at room temperature in the absence of ionizing radiation.

TABLE IV

BLANK EXPERIMENTS OF CYANOGEN-ORGANIC MIXTURES

Blank Experiment No.	Organic Compound	Cyanogen (Moles)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)
1	2,4,4-Trimethyl-pentene-1 (0.160)	0.0226	0.0225	0.0001
2	n-Heptane (0.171)	0.0280	0.0276	0.0004

H. Quantitative Determination of the Solubility of Cyanogen in Organic Compounds

The solubility studies were made in a tube (4.2 x 10.5 cm) fitted with a ground glass cap (45/50 standard taper) to which a stopcock and U-manometer were attached.

In the determination of the solubility of cyanogen in an organic compound, the organic compound was placed in the solubility apparatus, which was at dry ice-acetone temperature. The cyanogen was transferred as a solid to the apparatus, and the mixture was allowed to equilibrate partially at 5° to 7° C in a water bath. The mixture was then placed in a constant temperature bath at 25.0° C and allowed to equilibrate until there was no pressure build-up as indicated by the mercury U-manometer. The cyanogen was then determined by the previously

mentioned method of extracting the cyanogen with aqueous potassium hydroxide and titrating with standard silver nitrate the potassium cyanide formed. The solubilities are reported in milliliters of cyanogen, at standard temperature and pressure, per milliliter of organic compound and are summarized in Table V.

TABLE V

SOLUBILITY OF CYANOGEN IN ORGANIC LIQUIDS AT 25.0° C

Compound	Mole Cyanogen/10 ml Organic	ml Cyanogen/ml Organic
Benzene[a]	0.0144	32.2 ± 0.6
Toluene	0.0156	35.0 ± 0.2
Cyclohexane	0.0079	17.7 ± 0.2
n-Heptane	0.0091	20.4 ± 0.2
2,4,4-Trimethyl-pentene-1	0.0105	23.5 ± 0.1
2,2,4-Trimethyl-pentane	0.0091	20.4 ± 0.4

[a]M. Berthelot, Ann. Chem. Phys. (8), 3, 146 (1904) reported for benzene 28 ml at standard temperature and pressure of cyanogen per milliliter of benzene at 20° C.

I. Gas-Chromatographic Application

A Perkin-Elmer vapor fractometer, Model 154D, has been obtained and investigations conducted to determine a suitable column packing for use in the analysis of cyanogen and the radiolysis products. The ideal column would be one which would separate hydrogen, cyanogen, hydrogen cyanide, and the volatile hydrocarbons. It was found that a 12-foot by 1/4-inch copper tubing column of 20 per

cent, by weight, tri-tolyl phosphate on Chromosorb P separated the higher molecular weight irradiation products, but it was not suitable for the lower molecular weight products. A 6-foot column of silica gel was not suitable because it absorbed cyanogen. A 20-foot molecular sieve column was also unsuitable. A 15-foot column of Kel-F, a fluoro-ethylene polymer, on Chromosorb P is now under investigation.

III. DISCUSSION

A. Preparation and Handling of Cyanogen

Due to the extreme toxicity of cyanogen, careful attention was given to the procedures, apparatus, and equipment used in the preparation and handling of cyanogen such that hazards have been reduced to a minimum. All preparations and the handling of cyanogen are carried out in a well-ventilated hood. The irradiation glass tubes are sealed and contained in a brass irradiation tube-holder during the irradiations in the irradiator. The brass tube-holder is designed so it will be continuously evacuated during an irradiation. In the event of breakage, gaseous material would therefore be evacuated and exhausted to a hood. Also, any spillage of liquid would be confined to the brass tube-holder. The same precautions are used in the irradiations of cyanogen-organic mixtures in the stainless steel bomb.

B. Irradiations

Several representative hydrocarbons--benzene, toluene, n-heptane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane and cyclohexane--have been irradiated in admixture with cyanogen. The conditions and results of the irradiations are summarized in Tables I, II and III.

The irradiated mixtures were separated by distillation into two fractions: (1) lower molecular weight radiolysis products plus most of the hydrocarbon and (2) higher molecular weight radiolysis products. These fractions have been analyzed by infrared spectra primarily to determine if any cyano products were present. The infrared spectra of the lower molecular weight radiolysis products plus most of the original hydrocarbon from each irradiation were identical to, or very similar to, that of the pure hydrocarbons. The absence of absorption in the 4.4-micron region indicates either that no radiation-induced cyanogenation occurred to produce cyano products more volatile than the parent hydrocarbon or that the cyano products were present in such small amounts as to escape detection. The infrared spectra of the higher molecular weight radiolysis products from the irradiated mixtures of toluene, n-heptane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, and cyclohexane showed an absorption band at 4.4 microns which is attributed to the cyano group (-CN). Benzene did not exhibit any evidence of cyanogenation until a mixture with a mole ratio of 3:1 (benzene:cyanogen) in the stainless steel bomb was irradiated. Absorption peaks at 2.92 microns in irradiations 10, 11, 12 and 15 (Table II)suggest the possibility of the presence of an amine group in these radiolysis products. The absorption at 4.4 microns indicated very strongly that radiation-induced cyanogenation to produce products of higher molecular weight than the hydrocarbon has taken place with the above-mentioned organic compounds. The presence of the amine group suggests that some of the cyano product has been reduced to the amine during irradiation.

In all irradiations of mixtures of benzene and cyanogen prior to the use of the stainless steel bomb, no evidence was obtained that any cyanogenation

had occurred. With a stainless steel bomb, a mixture of cyanogen and benzene in a molar ratio of one to three was irradiated. This ratio of cyanogen to benzene was much higher than any used in prior irradiations. The infrared spectra of the gross radiolysis products which were higher boiling than benzene showed strong absorption at 4.4 microns. This infrared spectra compared very favorably with the infrared spectra of a solution of 10 per cent benzonitrile in benzene, and very few of the characteristics of the infrared spectra of irradiated benzene were observed.

Several mixtures of cyanogen-cyclohexane with varying amounts of cyanogen were irradiated (Tables I, II, and III). The cyanogen consumed in three of the irradiations was approximately the same (0.011 mole) even though the amount of cyanogen varied from 0.0116 to 0.0167 mole. In one irradiation, 0.0297 mole of cyanogen was used and 0.0240 mole of cyanogen consumed. After removal of the cyclohexane from the irradiated mixtures, the flask residues, 1.426 gm, were combined and distilled at 260° C and 2 mm pressure. The distillate, 0.328 gm, was a clear yellow liquid showing a very strong cyano infrared absorption band at 4.4 microns. Absorption at 2.92 and 3.07 microns is possibly due to amine groups. The presence of these bands suggest that some reduction of the cyano product to an amine group occurs during irradiation.

C. Blank Experiments

The results of the two blank experiments showed that no reaction of cyanogen with either n-heptane or 2,4,4-trimethylpentene-1 occurred. The results of the blank experiments are given in Table IV.

D. Solubilities of Cyanogen

The solubilities of cyanogen in the hydrocarbons used in the irradiations have been determined at 25.0° C. This information was needed to determine the amounts of cyanogen that could be mixed with the hydrocarbon and safely irradiated. From the data, Table V, cyanogen shows increasing solubility in the classes of hydrocarbons in the following order: cycloalkanes, alkanes, alkenes and aromatics.

IV. SUMMARY

Forty-four irradiations have been completed in the period covered by this report. These irradiations consisted of 35 of cyanogen-hydrocarbon mixtures, 8 of pure hydrocarbons, and 1 of pure cyanogen. The infrared spectra of the higher molecular weight radiolysis products from benzene, toluene, n-heptane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, and cyclohexane had absorption bands at 4.4 microns, which can be attributed to the presence of the cyano group. The absorption at 4.4 microns (cyano group) is evidence that radiation-induced cyanogenation has taken place with these hydrocarbons. Under the conditions employed, there is no evidence that any cyano products were formed with benzene at low cyanogen-to-benzene concentration ratios.

The solubilities of cyanogen in the hydrocarbons used in the irradiations have been determined. The solubility of cyanogen in the various classes of hydrocarbons shows increases in the following order: cycloalkanes, alkanes, alkenes, and aromatics.

Dosimetry determinations, employing the same geometry as used in the irra-

diations, have been made with the ferrous ion dosimeter in holes Nos. 1, 11, and 12 of the irradiator. The dose rates for the holes were found to be: (a) No. 1, $(7.59 \pm 0.12) \times 10^5$ rad/hr; (b) No. 11, $(7.62 \pm 0.15) \times 10^5$ rad/hr; and (c) No. 12, $(8.89 \pm 0.09) \times 10^5$ rad/hr. Dosimetry of the center hole with the stainless steel bomb was found to be $(1.01 \pm 0.01) \times 10^6$ rad/hr.

A gas chromatographic unit has been obtained and will be used in analysis of the radiolysis products of the irradiated mixtures of cyanogen-organic compounds. Column packings suitable for the analysis of cyanogen and the radiolysis products are now being tested.

A manuscript, "Irradiation of Cyanogen-Hydrocarbon Mixtures with Ionizing Radiation," has been prepared (see the Appendix). Permission to submit this manuscript to an appropriate scientific journal for publication has been requested from the Savannah River Operations Office, Aiken, South Carolina.

V. FUTURE PROGRAM

The proposed research for the coming year will be concentrated on the following:

1. Emphasis will be placed on studying in detail the radiation chemistry of mixtures of cyanogen with one or more specific hydrocarbons. Particular attention will be given to the characterization of the radiolysis products and obtaining G values, particularly for cyano products. The following variables will be investigated: varying ratios of cyanogenating reagent to organic compound, temperature, and pressure within certain limits; varying lengths of irradiation times; and the use of possible catalytic agents. Feasible mechanisms will be postulated from the experimental data.

2. Irradiations of mixtures of cyanogen with a number of hydrocarbons in a stainless steel bomb will be made. The use of the steel bomb will permit larger amounts of cyanogen to be used than have been used with the glass irradiation tubes.

3. Emphasis will be placed on a more complete characterization of the radiolysis products. Gas chromatography, infrared spectroscopy, and other analytical methods that are applicable will be employed in this phase of the work.

4. Consideration will be given to some irradiations with other possible cyanogenating reagents.

5. Consideration will be given to initiating some irradiation studies of mixtures of hydrogen cyanide and alkenes.

Respectfully submitted:

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Approved:

Fred Sicilio
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VI. APPENDIX

IRRADIATION OF

CYANOGEN-HYDROCARBON MIXTURES WITH IONIZING RADIATION

IRRADIATION OF CYANOGEN-HYDROCARBON MIXTURES WITH IONIZING RADIATION

by

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This is a preliminary report on a study of the radiation chemistry of cyanogen-hydrocarbon mixtures. This study was undertaken to investigate the feasibility of effecting with high energy radiation direct cyanogenation of hydrocarbons with cyanogen and other cyanating reagents and to study the mechanism of the reaction. There are very few reports of direct cyanogenation of organic compounds. Janz[1] reported on the direct thermal cyanogena-

(1) G. Janz, J. Am. Chem. Soc., 74, 4529 (1952).

tion of benzene with cyanogen and that the best conditions were 740° C and 2-3 seconds contact time with cyanogen in excess. McKusick, et al[2], reported

(2) B. C. McKusick, W. E. Mochel and F. W. Stacey, ibid, 82, 723 (1960).

on the cyanogenation, effected by 2-mev electrons, of benzene, toluene and cyclohexane with hydrogen cyanide. In this investigation a number of representative hydrocarbons have been irradiated in admixture with cyanogen. These irradiated mixtures have been examined with infrared spectroscopy primarily for the presence of gross cyano products.

Experimental

Hydrocarbons. - The hydrocarbons used in this work were either reagent grade or Phillips pure grade, and were used without further purification.

Cyanogen. - The method, employed by Janz,[3] of treating dry $CuSO_4 \cdot 5H_2O$ with an excess of a saturated solution of sodium cyanide was used for the synthesis of cyanogen.

(3) G. Janz, Inorganic Synthesis, edited by T. Moeller, McGraw-Hill Co., Inc., New York, N. Y. (1957), Vol. V, p. 43.

Radiation Source. - The mixtures were irradiated in a 12 kilocurie Cs-137 source.[4] The ferrous-ion dosimeter was employed, and dosimetry studies were made so that essentially the same geometry was obtained as in the irradiations.

(4) R. C. Palmer and R. W. Carter, J. Appd. Rad. and Isotopes (in press).

Irradiations. - A typical sample for irradiation was prepared by introducing a known amount of the hydrocarbon into a previously weighed glass irradiation tube at -78° C. Solid cyanogen was added, and the irradiation tube sealed and weighed. The amount of cyanogen was obtained by difference. After exposure to the γ-radiation for the desired time period, the irradiated mixture was removed and treated with 1M KOH. After separation of the organic and aqueous phases, the KCN formed was titrated with standard $AgNO_3$ solution.[5]

(5) F. H. Rhodes, J. Ind. and Eng. Chem., 4, 652 (1912).

The organic phase was then dried with magnesium sulfate, filtered and distilled to separate the low-boiling products and original hydrocarbon from the products less volatile than the original hydrocarbon. Infrared spectra were obtained on both distillate and the higher boiling products. Pure hydrocarbons were irradiated in the same manner as the mixtures, and infrared spectra obtained on the irradiated material for comparison.

Blank Experiments. - Two mixtures, cyanogen--n-heptane and cyanogen--2, 4, 4-trimethylpentene-1, were prepared in the same manner as for irradiation. These mixtures, after standing at room temperature for 168 hours, were treated in the same manner as an irradiated mixture. The amount of cyanogen remaining was determined and infrared spectra obtained. The results showed that no reaction occurred in the absence of the ionizing radiation.

Results and Discussion

Some of the irradiations of the hydrocarbons in admixture with cyanogen are listed in Table I:

TABLE I

IRRADIATIONS OF CYANOGEN-HYDROCARBON MIXTURES

Irradiation Mixture[a]				
	Hydrocarbon (Moles)	Cyanogen (Moles)	Cyanogen Consumed (Per Cent)	Dose (ev/gm)
n-Heptane	0.171	0.0065	54	8.9×10^{21}
2-Methylpentane	0.206	0.022	42	8.9×10^{21}
3-Methylhexane	0.172	0.030	33	7.7×10^{21}
2,2,4-Trimethylpentane	0.152	0.016	20	8.9×10^{21}
2,4,4-Trimethylpentene-1	0.150	0.0306	26	8.9×10^{21}
Cyclohexane	0.232	0.0116	97	8.9×10^{21}
Toluene	0.235	0.0119	78	7.7×10^{21}
Benzene	0.225	0.0784	49	1.0×10^{22}

[a]All mixtures were exposed for 168 hours. All irradiations were carried out in sealed Pyrex glass tubes except benzene-cyanogen, which was carried out in a stainless steel bomb.

Infrared spectra were obtained on the pure hydrocarbons, the irradiated hydrocarbons, and the two fractions obtained from the distillation of the irradiated cyanogen-hydrocarbon mixtures. These two fractions were (1) the distillate which contained the lower boiling radiolysis products with most of the original hydrocarbon and (2) the higher boiling radiolysis products. Absorption in the 4.35 to 5.00 micron region of the infrared spectra is attributed

to the -C≡N group.[6] Absorption in this range was absent in the spectra of the

(6) L. J. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley and Sons, Inc., New York, N. Y. (1958) 2nd edition, p. 263.

pure hydrocarbons, the irradiated hydrocarbons, and the distillate of the irradiated cyanogen-hydrocarbon mixtures. The infrared spectra of the higher boiling fraction from each irradiated cyanogen-hydrocarbon mixture showed a very strong absorption band at approximately 4.40 microns. This is strong evidence that radiation-induced cyanogenation occurred with the parent hydrocarbon and/or some higher boiling radiolysis product to give cyano-radiolysis products. The absence of absorption in the same region of the spectra of the lower boiling radiolysis products of the irradiated cyanogen-hydrocarbon mixtures indicates either that no radiation-induced cyanogenation occurred to produce cyano products more volatile than the parent hydrocarbon or that the cyano products were present in such small amounts as to escape detection.

The higher boiling radiolysis material from several irradiated cyanogen-cyclohexane mixtures were combined, giving a total of 1.43 g. This material was distilled at 260° C and 2 mm pressure, giving a clear yellow distillate. The infrared spectra of this distillate had a very strong absorption band at 4.40 microns. A nitrogen analysis gave a value of 4.66 per cent. This higher boiling radiolysis product is evidently a mixture.

Several irradiations of benzene were carried out in Pyrex glass tubes. There was no evidence of any cyano products from the infrared spectra of the products of these irradiations. However, an irradiation of a cyanogen-benzene mixture in a stainless steel bomb gave a higher boiling radiolysis material of which the infra-

red spectra showed strong absorption at 4.40 microns. The stainless steel bomb permitted a higher ratio of cyanogen to benzene to be used than possible with the glass irradiation tubes. The infrared spectra of the higher boiling radiolysis product from the cyanogen-toluene irradiation in a glass tube showed absorption at 4.4 microns. This suggests in the case of toluene that the cyanogenation has occurred at the methyl group.

The results are as yet too fragmentary to suggest any mechanism for the reaction. Studies are continuing with specific hydrocarbons and the results will be reported in subsequent papers.

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RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

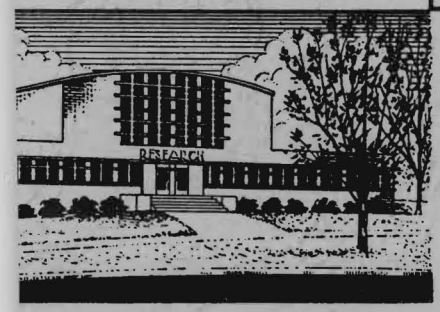
By

James A. Knight, Jr.

Prepared For

THE DIVISION OF ISOTOPES DEVELOPMENT
UNITED STATES ATOMIC ENERGY COMMISSION

20 April 1962



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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of the Georgia Institute of Technology
Atlanta, Georgia

ANNUAL TECHNICAL STATUS REPORT NO. 2

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

COVERING THE PERIOD
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Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

The overall broad objectives of this research program are to study the effects of ionizing radiation on the cyanogenation of organic compounds. During the period covered by this report, emphasis was placed on: (1) the irradiation of pure cyclohexane and mixtures of cyanogen-cyclohexane; and (2) the analysis of the irradiated samples for total gases, cyclohexene, dicyclohexyl and cyclohexyl cyanide with gas chromatography. All samples were irradiated in sealed glass irradiation tubes in the 12-kilocurie Cesium-137 Research Irradiator.

From the results to date, the G values for both cyclohexene and dicyclohexyl from pure cyclohexane decrease with increasing dose. The G values for cyclohexene from the mixtures are approximately one-half of the G values from pure cyclohexane for a given total dose. The G values for dicyclohexyl from the mixtures are about constant with varying dose, but are considerably less than the G values for dicyclohexyl from pure cyclohexane. Cyclohexyl cyanide has been identified by gas chromatographic methods as one of the products from cyanogen-cyclohexane mixtures. There is qualitative evidence that hydrogen cyanide is present in the gaseous products from the mixtures.

TABLE OF CONTENTS

This report contains 8 pages.

LIST OF TABLES

I. INTRODUCTION

This report summarizes the work performed from April 1, 1961, to March 31, 1962 and is submitted as the second annual report. The program since July 1, 1961, has been at a reduced level as Mr. Richard Stokes, the research assistant, was employed for three-fourths time on the project instead of full time. The purpose of the research under this contract is to study radiation-induced cyanogenation of organic compounds, with interest in both the products of the reactions and in the mechanisms of the reactions.

During the period covered by this report the system, cyanogen-cyclohexane, was selected for a more detailed study. Irradiations were made of pure cyclohexane and of mixtures of cyanogen-cyclohexane for comparison purposes. Cyclohexane was selected for the initial study for the following reasons:

(a) The radiation chemistry of cyclohexane has been reported in considerable detail in the literature.

(b) There are three major radiolysis products - hydrogen, cyclohexene and dicyclohexyl - from cyclohexane.

(c) Cyclohexane and cyanogen would form only one mono cyano product, i.e. cyclohexyl cyanide.

Gas chromatographic analysis has been utilized in this phase of the program for the qualitative and quantitative determination of the major radiolysis products.

II. EXPERIMENTAL WORK

A. Cyanogen

Cyanogen of 99 per cent purity or better is now commercially available and has been used without further purification in the irradiations since November 1961.

B. Preparation of Samples for Irradiation

1. Cyclohexane

The cyclohexane in the irradiation tube is degassed by repeating several times the cycle of freezing (−70° C), evacuation, and melting under vacuum. The irradiation tube is then sealed under vacuum.

2. Cyanogen-Cyclohexane Mixtures

In the preparation of mixtures for irradiation, the cyclohexane is degassed as described above. The necessary amount of cyanogen from the cylinder is measured in a gas burette. The irradiation tube containing the cyclohexane is cooled with liquid nitrogen, and the cyanogen is transferred from the burette to the irradiation tube by a combination of distillation and displacement with mercury. The irradiation tube is then sealed under vacuum.

C. Dosimetry

The center hole of the Cesium-137 Research Irradiator has been utilized since November 1, 1961, for irradiations for quantitative purposes. The dose in the center hole was determined with the ferrous ion dosimeter employing essentially the same geometry as used during irradiations. This dose was determined for 10 ml of dosimetry solution to be 7.77×10^{19} ev/gm/hr.

D. Gas Chromatography

1. Analysis for Radiolysis Products

The radiolysis products from cyclohexane and cyanogen-cyclohexane mixtures can be divided into three groups: gaseous, intermediate, and higher molecular weight. The major radiolysis products from cyclohexane are hydrogen, cyclohexene and dicyclohexyl. From mixtures of cyanogen-cyclohexane, the major

additional product identified to date is cyclohexyl cyanide.

Several column packings have been tested for characterization of the radiolysis products. To date, the most satisfactory column and conditions for analysis of the liquid products are as follows:

(a) Cyclohexene - a 12 foot 1/4 inch OD column packed with 20 per cent tricresyl phosphate by weight on 30/60 mesh Chromosorb at 82° C.

(b) Dicyclohexyl and cyclohexyl cyanide - a 6 foot 1/4 inch OD column packed with 20 percent Ucon oil LB-550-X by weight on 60/80 mesh Chromosorb at 198° C.

(c) Gaseous products - Several column packings have been tested for analysis of the gaseous radiolysis products, but no one packing has proved completely satisfactory.

2. Calibrations

The gas chromatographic unit has been calibrated for thermal response to cyclohexene, dicyclohexyl and cyclohexyl cyanide with dilute solutions of the respective compounds in cyclohexane. The gas chromatographic conditions were the same as the conditions used for analysis. All injections were made with a Hamilton microliter syringe. The areas were measured with a planimeter.

E. Irradiations

A number of irradiations of pure cyclohexane and cyanogen-cyclohexane were performed in the outside holes of the Cesium-137 Research Irradiator for the purpose of working out techniques for analysis of the radiolysis products. Preliminary quantitative results from these irradiations did not give reproducible values. Therefore, all irradiations since November 1961 have been performed in the center hole. The results from the irradiations

of pure cyclohexane are listed in Table I and from the irradiations of cyanogen-cyclohexane mixtures are listed in Table II.

TABLE I

G VALUES FROM CYCLOHEXANE

Irradiation Number[a]	Cyclohexane (gm)	Dose (ev/gm)	G Values[b] Gases[c]	Cyclohexene	Dicyclohexyl
67	9.6	2.87×10^{20}	--[d]	2.0	--[e]
68	9.3	2.87×10^{20}	--	2.0	--
69	7.8	2.87×10^{20}	--	2.1	--
71	7.9	2.31×10^{20}	--	2.2	1.4
76	8.2	2.44×10^{20}	3.2	2.2	1.6
85	7.8	2.44×10^{20}	3.7	2.3	1.5
72	8.0	4.89×10^{20}	4.2	1.7	1.4
77	8.2	4.89×10^{20}	5.3	1.6	1.3
73	7.9	1.47×10^{21}	5.1	0.95	1.0
84	7.7	1.47×10^{21}	4.1	0.93	0.95

[a] All irradiations were performed in the center sample hole of the Cesium-137 Research Irradiator.

[b] The dose was determined with the ferrous ion dosimeter and electron density correction applied.

[c] The gases are reported to be at least 95 per cent hydrogen.

[d] The gases from irradiations 67 through 71 were not determined.

[e] The dicyclohexyl was not determined for irradiations 67, 68 and 69.

TABLE II

G VALUES FROM CYANOGEN-CYCLOHEXANE MIXTURES

Irradiation Number[a]	Mixture		Dose (ev/gm)	G Values[b]	
	Cyclohexane (gm)	Cyanogen (cc @ STP)		Cyclohexene	Dicyclohexyl
82	7.9	90	2.44×10^{20}	0.98	0.36
86	7.7	87	2.44×10^{20}	1.2	0.34
81	7.9	90	4.89×10^{20}	0.72	0.36
88	7.8	102	4.89×10^{20}	0.81	0.36
79	8.3	87	1.47×10^{21}	0.56	0.45
80	8.1	91	1.47×10^{21}	0.52	0.45

[a] All irradiations were performed in the center sample hole of the Cesium-137 Research Irradiator.

[b] The dose was determined with the ferrous ion dosimeter and electron density correction applied.

III. DISCUSSION

A. General Statement

The system, cyanogen-cyclohexane, has been selected for a detailed study of the radiation-induced cyanogenation process. A comparison is to be made of the effect of cyanogen on the major radiolysis products of cyclohexane. Pure samples of cyclohexane and mixtures of cyanogen-cyclohexane have been irradiated with this purpose in mind. Analyses of the irradiated pure samples have been made for total gases, cyclohexene and dicyclohexyl. For the mixtures analyses have been made for cyclohexyl cyanide also.

B. Radiolysis Products from Pure Cyclohexane

G values for hydrogen from cyclohexane are reported in the literature in the range of about 5.0 to 5.4. The G values obtained to date for gaseous products (at least 95 per cent hydrogen) in our work vary from 3.2 to 5.3. Additional experimental work will be performed on the gaseous products in an effort to obtain more reproducible and satisfactory results.

G values for cyclohexene and dicyclohexyl from cyclohexane are reported in the literature in the range of about 2.2 to 2.5 and of about 1.4 to 2.0 respectively. The G values obtained to date for cyclohexene vary from 2.25 with a total dose of 2.44×10^{20} ev/gm to 0.93 with a total dose of 1.47×10^{21} ev/gm. G values for dicyclohexyl obtained to date vary from 1.5 with a total dose of 2.44×10^{20} ev/gm to 0.98 with a total dose of 1.47×10^{21} ev/gm. In both cases the G values decrease with increasing dose.

C. Radiolysis Products from Mixtures of Cyanogen-Cyclohexane

The gaseous radiolytic products from mixtures of cyanogen-cyclohexane might contain, in addition to hydrogen and hydrocarbon gases, hydrogen cyanide and cyanogen. Several columns were tested in an effort to find one suitable for the analysis of the expected gaseous mixture. To date, no particular column or set of conditions has proven entirely satisfactory. The columns tested included a silica gel column at 32° and 60° C, a 12 foot tetraisobutylene column at 0°, a 12 foot tricresylphosphate column at 32° C, and a 25 foot tricresylphophate column at 0° C. The 12 foot tetraisobutylene column and the 25 foot tricresylphosphate column are the most promising, although neither is ideal. Analysis of the gaseous products from irradiations 80, 81 and 82 with the 25 foot column showed the presence of hydrogen cyanide and cyanogen. Additional work will be done with the gaseous products in an

effort to obtain satisfactory analysis and G values by chromatographic methods.

G values for cyclohexene and dicyclohexyl are given in Table II. The G values for cyclohexene decrease with increasing dose as in the case of pure cyclohexane. A comparison of the G values shows also that the G values for cyclohexene from the mixtures are approximately one-half of the G values from pure cyclohexane. The G values for dicyclohexyl from the mixtures are about constant with varying dose, but are considerably less than the G values for dicyclohexyl from pure cyclohexane. Cyclohexyl cyanide has been identified as a product from the mixtures, but reproducible G values have not been obtained.

IV. Summary

The main emphasis has been on a detailed study of the radiation chemistry of cyanogen-cyclohexane mixtures. From the results to date, the G values for both cyclohexene and dicyclohexyl from pure cyclohexane decrease with increasing dose. The G values for cyclohexene and dicyclohexyl from cyanogen-cyclohexane mixtures are lower than from pure cyclohexane. Also the G values for cyclohexene from the mixtures decrease with increasing dose whereas the G values for dicyclohexyl do not. Cyclohexyl cyanide has been identified by gas chromatography as one of the products from cyanogen-cyclohexane mixtures. There is qualitative evidence that hydrogen cyanide is present in the gaseous products from the mixtures.

V. FUTURE PROGRAM

The proposed research for the period April 1, 1962, to October 31, 1962, will be concentrated on the following:

1. Emphasis will continue to be placed on the detailed study of the

radiation chemistry of cyanogen-cyclohexane mixtures. Particular attention will be given to the characterization of the radiolysis products and to obtaining G values, particularly for cyano products. The following variables will be investigated: varying ratios of cyanogen to cyclohexane, varying lengths of irradiation times, and the use of possible catalytic agents.

2. Emphasis will be placed on a more complete characterization of the radiolysis products. Gas chromatography and other analytical methods that are applicable will be employed in this phase of the work.

Respectfully submitted:

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Project Director

Approved:

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FINAL REPORT SRO-78

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By James A. Knight, Jr.

Prepared for
United States Atomic Energy Commission
Division of Isotopes Development
Germantown, Maryland

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28 February

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
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Atlanta, Georgia

FINAL REPORT

PROJECT NO. A-446-8

RADIATION-INDUCED CYANOGENATION OF ORGANIC COMPOUNDS

By

JAMES A. KNIGHT, JR.

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Placed By
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AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

The hydrocarbons--benzene, toluene, n-heptane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, and cyclohexane--were irradiated in a 12-kilocurie cesium-137 source in admixture with cyanogen. Based on infrared spectra of samples of the irradiated mixtures, it was concluded that radiation-induced cyanogenation did occur under the conditions employed with each of the hydrocarbons.

The radiolysis of the cyanogen-cyclohexane system was examined in more detail. Gas chromatography was used to analyze for the major radiolysis products from irradiated pure cyclohexane and mixtures of cyanogen-cyclohexane. The G values for hydrogen from the mixtures were less than 4. The G values for hydrogen cyanide for the samples analyzed were approximately 2. The G values for cyclohexene from the mixtures varied from 1.1 for 2.44×10^{20} ev/gm to 0.55 for 1.46×10^{21} ev/gm and were about 50 per cent of the G values from pure cyclohexane for corresponding doses. The G values for dicyclohexyl from the mixtures were approximately 0.4 for all doses, whereas the G values from pure cyclohexane decreased from 1.57 for 2.44×10^{20} ev/gm to 0.99 for 1.46×10^{21} ev/gm. The G values for cyclohexyl cyanide, obtained by analyzing different irradiated mixtures immediately after irradiation, varied from 3.9 to 10.1 for a dose of 2.44×10^{20} ev/gm. Samples of these same irradiated mixtures, after treatment with potassium hydroxide solution, gave G values of 14 to 18, and after treatment with potassium hydroxide pellets, gave G values of 18 to 20 for cyclohexyl cyanide. The available evidence indicates that a considerable amount of the cyclohexyl cyanide in these irradiated mixtures was combined in some type of "complex" which was destroyed by treatment with base. The data are insufficient to warrant the postulation of any mechanisms for the radiolysis of the cyanogen-cyclohexane system.

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I. INTRODUCTION

This is a report on the work performed from 1 May 1960 to 28 February 1963. The purpose of the research under this contract was to study radiation-induced cyanogenation of organic compounds. Cyanogen was used as the cyanogenating agent in all of the irradiations and a number of hydrocarbons including straight chain, branched, unsaturated, and aromatic compounds were irradiated in admixture with cyanogen. The irradiation source was a 12-kilocurie cesium-137 source.[1]

There are many indirect chemical methods for the preparation of cyano organic compounds but few reports of direct cyanogenation. Mowry[2] has given an excellent review of chemical methods for the introduction of the cyano group into various organic compounds. The direct thermal cyanogenation of benzene has been reported.[3] The best conditions for the reaction were reported to be 740° C and 2 to 3 seconds contact time with cyanogen in excess. The direct cyanogenation of benzene, toluene, and cyclohexane with hydrogen cyanide effected by 2 Mev electrons has been reported.[4]

The first phase of the program was concerned with determining if radiation-induced cyanogenation did occur between cyanogen and representative hydrocarbons, which were n-heptane, 2-methylpentane, 3-methylhexane, 2,2,4-trimethylpentane,

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[1] R. W. Carter, R. C. Palmer and W. V. Willis, "Cesium-137 Research Irradiator," Final Report, Division of Isotopes Development, United States Atomic Energy Commission, SRO-46.

[2] D. T. Mowry, Chemical Reviews, 42, 189 (1948).

[3] G. Janz, J. Am. Chem. Soc., 74, 4529 (1952).

[4] B. C. McKusick, W. E. Mochel and F. W. Stacey, J. Am. Chem. Soc., 82, 723 (1960).

2,4,4-trimethylpentene-1, benzene, toluene and cyclohexane. Infrared spectra of the irradiated mixtures gave good evidence that radiation-induced cyanogenation did occur under the conditions employed with each of the hydrocarbons tested.

As the first phase of the program gave good evidence that cyanogenation did occur in the irradiations of the mixtures of cyanogen with the hydrocarbons used, it was decided to investigate in more detail the system of cyclohexane and cyanogen. This represents the second phase of the program. Cyclohexane was selected for this study for the following reasons:

(a) The radiation chemistry of cyclohexane has been reported in considerable detail in the literature.

(b) There are three major radiolysis products--hydrogen, cyclohexene, and dicyclohexyl--from cyclohexane.

(c) Cyclohexane and cyanogen would form only one mono cyano product, i.e. cyclohexyl cyanide.

Gas chromatographic analysis was utilized in this second phase of the program for the qualitative and quantitative determination of the major radiolysis products.

In order to determine if any detectable cyanogenation would occur at room temperature in the absence of high energy radiation, two blank runs, cyanogen--n-heptane and cyanogen--2,4,4-trimethylpentene-1, were made. The cyanogen-hydrocarbon mixtures were sealed in reaction tubes and allowed to stand at room temperature for 168 hours. No reaction occurred in either mixture.

II. EXPERIMENTAL

A. Hydrocarbons

The hydrocarbons used in this work were either reagent grade or Phillips research grade and were used without further purification.

B. Cyanogen

In the first part of the program, cyanogen was prepared by the method employed by Janz.[5] This method consisted of treating dry copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) with an excess of a saturated solution of sodium cyanide. The preparation was carried out in an all-glass apparatus in a well-ventilated hood. The rate of evolution of cyanogen was controlled by carefully regulating the addition of the saturated solution of sodium cyanide. During the preparation of cyanogen, the apparatus was continuously swept with nitrogen. The gases were bubbled through silver nitrate solution to remove any hydrogen cyanide and then passed through two drying towers of phosphorous pentoxide supported on glass wool. The cyanogen was condensed in a cold trap in a dry ice-acetone bath. The exhaust gases from the cold trap bubbled through a potassium hydroxide solution which removed any remaining cyanogen. The cyanogen was stored in a dry ice-acetone bath until needed.

During the course of this investigation, cyanogen of 99 per cent purity or better became available from the Matheson Company, and after November 1961, this cyanogen was used without further purification.

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[5] G. Janz, Inorganic Synthesis, edited by T. Moeller, McGraw-Hill Co., Inc., New York, N. Y. (1957), Vol. V., p. 43.

C. Radiation Source and Dosimetry

The 12-kilocurie cesium-137 source has been adequately described.[1] In the first phase of the program, a number of the outside samples holes were utilized. In the second phase all irradiations were performed in the center sample hold. The ferrous-ion dosimeter was employed, and dosimetry measurements were made so that essentially the same geometry was obtained as in the irradiations. In calculating G values for the cyclohexane irradiations, an electron density correction was applied, and it was assumed that the dose absorbed by the mixtures was due to the cyclohexane.

D. Preparation of Samples for Irradiations

1. Phase 1

The cyanogen-hydrocarbon mixtures for the irradiations for the first phase of the program were prepared by introducing a known amount of the hydrocarbon into a weighted glass irradiation tube at dry ice-acetone temperature. With a spatula cooled to about -78° C, solid cyanogen was added to the irradiation tube, and the tube sealed. The amount of cyanogen was obtained from the difference.

Some irradiations were carried out in a stainless steel bomb with a 30 ml capacity and dimensions of 1 inch outside diameter by 4 inches in length. The bomb was charged by transferring cyanogen directly into the bomb at -78° C, carefully adding a known weight of benzene and sealing with a brass valve.

2. Phase 2

In the preparation of cyanogen-cyclohexane mixtures, the cyclohexane in the irradiation tube was attached to a vacuum line and degassed by repeating

several times the cycle of freezing (about -78° C), evacuation, and melting under vacuum. The necessary amount of cyanogen from the cylinder was measured in a gas burette. The irradiation tube containing the cyclohexane was cooled with liquid nitrogen, and the cyanogen was transferred from the burette to the irradiation tube by a combination of distillation and displacement with mercury. The irradiation tube was sealed under vacuum.

Pure cyclohexane samples for irradiation were prepared by the same degassing procedure, and then sealed under vacuum.

E. Irradiations

The sealed sample for each irradiation was placed in a brass tube holder. The cap of the brass tube holder had an exhaust tube, and in all irradiations the brass tube holder was evacuated continuously during an irradiation. One end of a 15-foot section of small steel cable was soldered into the cap for lowering and raising the brass tube holder in the source. In the initial irradiations, the temperature during irradiation was monitored with a thermocouple. As there was no noticeable increase in the temperature of the sample during irradiation this practice was discontinued.

F. Analyses of the Irradiated Samples

1. Phase 1

a. Quantitative Determination of Cyanogen. It has been reported that cyanogen reacts quantitatively with sodium hydroxide or potassium hydroxide solutions to yield the alkali cyanide and cyanate.[6] This reaction formed the

[6] F. H. Rhodes, J. Ind. and Eng. Chem., 4, 652 (1912).

basis of the method for the quantitative determination of cyanogen. The cyanogen was reacted with an excess of 1M potassium hydroxide solution and the potassium cyanide formed was then titrated with standard silver nitrate solution to the first permanent turbidity. The addition of a small quantity of potassium iodide gave a sharper end-point.

b. Treatment of Irradiated Mixtures and Infrared Analyses. The irradiated contents of the glass irradiation tubes and bomb were treated as follows: The amount of cyanogen remaining after irradiation was determined by extraction with 1M potassium hydroxide solution and titrated as described in a above. The organic phase was then dried with magnesium sulfate, filtered, and distilled to give two fractions: (1) lower molecular weight radiolysis products plus most of the original hydrocarbon and (2) higher molecular weight radiolysis products plus a small amount of the original hydrocarbon.

Infrared spectra of both fractions and of the pure hydrocarbon were obtained with a Perkin-Elmer Model 221 infrared spectrophotometer. The spectra were compared and examined for absorption in the 4.4-micron region. Absorption in the 4.35- to 5.00-micron region is attributed to the cyanide (-C≡N) group.[7] Absorption in the infrared spectra of fraction 1--lower molecular weight radiolysis products plus most of the parent hydrocarbon--was absent. This indicated either that no radiation-induced cyanogenation occurred to produce cyano products more volatile than the parent hydrocarbon or that the cyano products were present in such small amounts as to escape detection. Absorption at 4.4

[7] L. J. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley and Sons, Inc., N. Y. 2nd Edition, p. 263 (1958).

microns was present in the infrared spectra of fraction 2--higher molecular weight radiolysis products--for most of the irradiations. The conditions and results of these irradiations are summarized in Table I.

TABLE I

IRRADIATIONS OF CYANOGEN-HYDROCARBON MIXTURES

Hydrocarbon (Moles)	Cyanogen (Moles) Initially	Cyanogen (Moles) Consumed	Dose[a] (ev/gm x 10^{-21})	Infrared Spectra Fraction 1[b]	Infrared Spectra Fraction 2
n-Heptane 0.171	0.0308	0.0193	3.8	Identical to pure n-heptane	Possible nitrile peak at 4.4 microns
n-Heptane 0.171	0.0065	0.0035	8.9	Very similar to pure n-heptane	Possible nitrile peak at 4.4 microns
2,2,4-Trimethylpentane 0.152	0.0164	0.0032	8.9	Very similar to pure 2,2,4-methylpentane	Possible nitrile peak at 4.4 microns
2,4,4-Trimethylpentene-1 0.150	0.0306	0.0079	8.9	Identical to pure 2,4,4-trimethylpentene-1	Possible nitrile peak at 4.4 microns
2-Methylpentane 0.206	0.0220	0.0093	8.9	Very similar to pure 2-methylpentane	Possible nitrile peak at 4.4 microns
3-Methylhexane 0.172	0.0298	0.0098	7.7	Very similar to pure 3-methylhexane	Possible nitrile peak at 4.4 microns
Cyclohexane[c] 0.232	0.0167	0.0110	8.9	Very similar to pure cyclohexane	Possible nitrile peak at 4.4 microns

(Continued)

TABLE I (Continued)

IRRADIATIONS OF CYANOGEN-HYDROCARBON MIXTURES

Cyclohexane 0.232	0.0116	0.0113	8.9	Very similar to pure cyclohexane	Possible nitrile peak at 4.4 microns
Toluene 0.246	0.0352	0.0285	1.3	Very similar to pure toluene	No nitrile peak observed
Toluene 0.235	0.0119	0.0092	7.7	Very similar to pure toluene	Possible nitrile peak at 4.4 microns
Benzene[d] 0.225	0.0078	0.0072	10	Identical to pure benzene	No nitrile peak observed
Benzene[e] 0.225	0.0784	0.0380	10	Identical to pure benzene	Possible nitrile peak at 4.4 microns

[a]Determined with ferrous ion dosimeter. Corrections for electron density were not made in the doses given in this table.

[b]Fraction 1 consisted of the lower molecular weight products plus most of the original hydrocarbon, and fraction 2 consisted of the higher molecular weight radiolysis products plus a small amount of the original hydrocarbon.

[c]A number of other irradiations of mixtures of cyanogen and cyclohexane were performed with varying amounts of cyanogen. The results were very similar.

[d]A number of other irradiations of mixtures of cyanogen and benzene were performed with varying amounts of cyanogen and with different doses. There was no evidence of radiation-induced cyanogenation from the infrared spectra.

[e]This irradiation was performed in a stainless steel bomb. All of the other irradiations were made in glass irradiation tubes.

2. Phase 2

a. Gas Chromatographic Units. The gas chromatographic units employed in this work were a 154-D Perkin-Elmer unit and a home-made unit. Both had thermal conductivity detectors with thermistors. Sargent Model SR recorders were used.

b. Gas Chromatographic Conditions. Gas chromatography was used to analyze both qualitatively and quantitatively for hydrogen, cyanogen, cyclohexane, cyclohexene, dicyclohexyl, and cyclohexyl cyanide. It was used to analyze qualitatively for hydrogen cyanide. The columns and conditions finally selected are given in Table II.

c. Calibrations. The instruments were calibrated for thermal response for substances which were analyzed quantitatively. For hydrogen, cyanogen, and cyclohexane, pure samples of known volume were used. For cyclohexene, dicyclohexyl, and cyclohexyl cyanide, individual dilute solutions of known concentration of each in cyclohexane were used. Hamilton microliter syringes with fixed needles were used for all sampling and calibration work. A planimeter was used to measure peak areas.

d. Sampling and Treatment of Irradiated Samples.

(1) Pure Cyclohexane. The irradiated cyclohexane was analyzed for hydrogen, cyclohexene, and dicyclohexyl. The irradiated sample was attached to a vacuum apparatus, and the gaseous products initially were analyzed by gas chromatography. Since the gas chromatographic analyses showed hydrogen to be essentially the only gaseous product, the hydrogen from later irradiations was

TABLE II

GAS CHROMATOGRAPHIC COLUMNS AND CONDITIONS

Substances Analyzed	Column[a]	Conditions[b] Column and Cell Temperature	Flow Rate (ml/min)
Hydrogen	5-ft silica gel coated with 2% di-2-ethylhexyl sebacate	47°	24
Hydrogen cyanide	25-ft 20% tetra-isobutylene on 50-60 mesh chromosorb	26° (column) 47° (cell)	30
Cyanogen Cyclohexane Cyclohexene	12-ft 20% tri-m-cresyl phosphate on 30-60 chromosorb	82°	40
Dicyclohexyl	9-ft 15% Ucon LB-550X on 50-60 mesh chromosorb	198°	50

[a]All columns were made of 1/4-inch copper tubing. The chromosorb was all acid washed Chromosorb P.

[b]Helium carrier gas was used for all substances except hydrogen, for which argon was used.

determined volumetrically. The liquid was analyzed with the gas chromatograph for cyclohexene and dicyclohexyl.

(2) Mixtures of Cyanogen-Cyclohexane. The irradiated sample was attached to a vacuum apparatus fitted with an open-end manometer, and the break-seal broken. After equilibration, samples of the gaseous mixture for gas chromatographic analyses were taken with a microliter syringe through a rubber septum.

The gaseous mixture contained hydrogen, hydrogen cyanide, cyanogen, and cyclohexane vapor. Gas chromatographic analysis of the liquid revealed--in addition to cyclohexane--cyanogen, cyclohexene, cyclohexyl cyanide, and dicyclohexyl.

Samples of some irradiated cyanogen-cyclohexane mixtures were treated immediately after irradiation by the methods outlined below and were then analyzed by gas chromatography for cyclohexyl cyanide at varying time intervals. The various treatments were:

(1) Approximately 2 ml of the irradiated mixture was washed with an equal volume of 5 per cent potassium hydroxide solution, washed free of base, and dried with anhydrous magnesium sulfate.

(2) Approximately 2 ml of the irradiated mixture was washed with an equal volume of 5 per cent hydrochloric acid, washed free of acid, and dried with anhydrous magnesium sulfate.

(3) Approximately 2 ml of the irradiated mixture was washed with an equal volume of 5 per cent potassium hydroxide followed by a wash with an equal volume of 5 per cent hydrochloric acid. The mixture was washed free of acid and dried with anhydrous magnesium sulfate.

(4) Approximately 2 ml of the irradiated mixture was washed with an equal volume of water and dried with anhydrous magnesium sulfate.

(5) Two potassium hydroxide pellets were added to approximately 2 ml of the irradiated mixture.

(6) A small sample of the irradiated mixture was retained without any treatment.

G. Blank Experiments

Two mixtures, cyanogen--n-heptane and cyanogen--2,4,4-trimethylpentene-1

were prepared in the same manner as samples for irradiation in phase 1. These mixtures, after standing at room temperature for 168 hours, were treated in the same manner as an irradiated mixture in phase 1. The amount of cyanogen remaining indicates that no reaction took place in either case (Table III). Gas chromatographic analysis of the organic phase from each experiment showed only the pure compound present. Infrared curves of the organic phase did not show any absorption that could be attributed to the cyano group. These results showed that no cyanogenation occurred at room temperature in the absence of high energy radiation.

TABLE III

BLANK EXPERIMENTS OF CYANOGEN-HYDROCARBON MIXTURES

Blank Experiment No.	Organic Compound (Moles)	Cyanogen (Moles)	Cyanogen Remaining (Moles)	Cyanogen Consumed (Moles)
1	2,4,4-Trimethyl-pentene-1 (0.160)	0.0226	0.0225	0.0001
2	n-Heptane (0.171)	0.0280	0.0276	0.0004

H. Preparation of Cyclohexyl Cyanide

A sample of cyclohexyl cyanide was prepared according to the procedure of Breslow and Hauser.[8] Cyclohexanecarboxylic acid, 66 gm, and 61 ml of

[8] D. S. Breslow and C. R. Hauser, J. Am. Chem. Soc., 67, 686 (1945).

thionyl chloride were refluxed on a steam bath for an hour. The reaction mixture was added to 600 ml of concentrated ammonium hydroxide cooled to 5° C. The temperature was not allowed to rise above 10° C during the addition. The solid amide was removed, washed with several portions of water and dried. The melting point of the amide was 185° C (uncorr.); yield, 37 gm.

The amide was refluxed overnight with 61 ml of thionyl chloride to convert it to the cyanide. The crude cyclohexyl cyanide was fractionally distilled at 19 mm; boiling point 77°-78° C; $n_D^{20°}$ 1.4534. Reported values:[9] boiling point 72°-73° C at 16 mm; $n_D^{19°}$ 1.4543.

I. Preparation of Cyclohexanemethylamine

Cyclohexanecarboxamide was prepared as described above and had a melting point of 182° C (literature[10] melting point 184° C). Reduction of the amide with lithium aluminum hydride gave the crude cyclohexanemethylamine.[11] The crude amine was fractionally distilled at 37 mm; boiling point 74°-75° C; $n_D^{20°}$ 1.4620. Reported values:[12] boiling point 74°-76° C at 35 mm; $n_D^{20°}$ 1.4630.

J. Solubility of Cyanogen in Hydrocarbons

The solubility of cyanogen in a number of hydrocarbons was determined quantitatively. The solubility studies were made in a tube (4.2 cm x 10.5 cm) fitted

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[9] C. A. 45: 1077 i.

[10] J. S. Lunsder, J. Chem. Soc., 87, 90 (1905).

[11] H. E. Baumgarten, F. A. Bower and T. T. Okamoto, J. Am. Chem. Soc., 79, 3145 (1957).

[12] R. A. Benkeser, et al, J. Am. Chem. Soc., 77, 6042 (1955).

with a ground glass cap (45/50 standard taper) to which a stopcock and U-manometer were attached.

In the determination of the solubility of cyanogen in a hydrocarbon, a known amount of the hydrocarbon was placed in the solubility apparatus which was at dry ice-acetone temperature. The cyanogen was transferred as a solid to the apparatus, and the mixture was allowed to equilibrate partially at 5° to 7° C in a water bath. The mixture was then placed in a constant temperature bath at 25.0° C and allowed to equilibrate until there was no pressure build-up as indicated by the mercury U-manometer. The cyanogen was then determined by the method, given in F above, of extracting the cyanogen with aqueous potassium hydroxide and titrating the potassium cyanide formed with standard silver nitrate. The solubilities are reported in milliliters of cyanogen at standard temperature and pressure per milliliter of organic compound and are summarized in Table IV.

TABLE IV

SOLUBILITY OF CYANOGEN IN HYDROCARBONS AT 25.0° C

Compound	Mole Cyanogen/10 ml Organic	ml Cyanogen/ml Organic
Benzene	0.0144	32.2 ± 0.6
Toluene	0.0156	35.0 ± 0.2
Cyclohexane	0.0079	17.7 ± 0.2
n-Heptane	0.0091	20.4 ± 0.2
2, 4, 4-Trimethylpentene-1	0.0105	23.5 ± 0.1
2, 2, 4-Trimethylpentane	0.0091	20.4 ± 0.4

III. RESULTS AND DISCUSSION

A. Phase 1

The first phase of the program was concerned with determining if radiation-induced cyanogenation did occur between cyanogen and representative hydrocarbons. Several representative hydrocarbons--benzene, toluene, n-heptane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, and cyclohexane--were irradiated in admixture with cyanogen. The conditions and results of these irradiations are summarized in Table I. Each irradiated sample was analyzed for remaining cyanogen. There was evidence that in nearly every irradiation some cyanogen remained, although the method of analysis would not distinguish between unreacted cyanogen and radiation-produced hydrogen cyanide. A brownish, insoluble material was formed in all irradiations and is evidence that not all of the cyanogen consumed was utilized in reacting with the hydrocarbon. This material was most likely polymerized cyanogen. For example, it has been reported that cyanogen irradiated by alpha-rays from radon yields a black polymer.[13] No attempts were made to characterize the brownish, insoluble material.

After determination of the remaining cyanogen, the irradiated mixtures were separated by distillation into fractions: (1) lower molecular weight radiolysis products plus most of the hydrocarbon and (2) higher molecular weight radiolysis products. These fractions were analyzed by infrared spectra primarily to determine if any cyano products were present. Absorption in the 4.35- to 5.00-micron region is attributed to the cyanide ($-C\equiv N$) group.[7] The infrared spectra of the lower molecular weight radiolysis products plus most of the

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[13] S. C. Lind, D. C. Bardwell and J. H. Perry, J. Am. Chem. Soc., 48, 1561, (1926).

original hydrocarbon from each irradiation were identical to, or very similar to, that of the pure hydrocarbons. The absence of absorption in the 4.4-micron region indicated either that no radiation-induced cyanogenation occurred to produce cyano products more volatile than the original hydrocarbon or that the cyano products were present in such small amounts as to escape detection. The infrared spectra of the higher molecular weight radiolysis products from the irradiated mixtures of toluene, n-heptane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, and cyclohexane showed an absorption band at 4.4 microns which is attributed to the cyano group (-C≡N). Benzene did not exhibit any evidence of cyanogenation until a mixture with a mole ratio of 3:1 (benzene:cyanogen) in a stainless steel bomb was irradiated. The absorption at 4.4 microns indicated very strongly that radiation-induced cyanogenation producing products of higher molecular weight than the hydrocarbon had taken place with the above-mentioned hydrocarbons.

In all irradiations of mixtures of benzene and cyanogen in glass irradiation tubes and prior to the use of a stainless steel bomb, no evidence was obtained that any cyanogenation had occurred. A stainless steel bomb was utilized for some irradiations so that a greater amount of cyanogen could be safely used. With the stainless steel bomb, a mixture of cyanogen and benzene in a molar ratio of one to three was irradiated. This ratio of cyanogen to benzene was much higher than any used in prior irradiations. The infrared spectra of the gross radiolysis products which were higher boiling than benzene showed strong absorption at 4.4 microns, compared very favorably with the infrared spectra of a solution of 10 per cent benzonitrile in benzene, and had very few of the characteristics of the infrared spectra of irradiated benzene.

In order to establish that no reaction occurred between cyanogen and hydro-

carbons at room temperature in the absence of high energy radiation, two samples were prepared in the same manner as for irradiation. The hydrocarbons used were n-heptane and 2,4,4-trimethylpentene-1. The mixtures, after standing at room temperature for 168 hours, were analyzed for cyanogen. The organic phase was analyzed by gas chromatography and infrared spectroscopy. The cyanogen remaining was equivalent, within experimental error, to the quantity added. The gas chromatographic analyses showed only the pure hydrocarbon present. The infrared spectra did not show any absorption that could be attributed to the cyano group. These results showed that no cyanogenation occurred at room temperature in the absence of ionizing radiation.

The solubilities of cyanogen in six of the hydrocarbons used in the irradiations were determined at 25.0° C. This information was needed to determine the amounts of cyanogen that could be mixed safely with the hydrocarbon and irradiated. From the data, Table IV, cyanogen showed increasing solubility in the classes of hydrocarbons in the following order: cycloalkanes, alkanes, alkenes, and aromatics.

From this phase of the study, it was determined that mixtures of cyanogen and several representative hydrocarbons could be safely irradiated in the 12-kilocurie cesium-137 source. It was also concluded based on the infrared spectra that radiation-induced cyanogenation did occur with each of the hydrocarbons tested. From the blank experiments it was evident that cyanogenation did not occur at room temperature in the absence of high energy radiation.

B. Phase 2

1. Results from Irradiated Cyclohexane

This phase of the investigation was devoted to a more detailed study

of the cyanogen-cyclohexane system. The reasons for selecting cyclohexane were given in the introduction. Samples of pure cyclohexane and mixtures of cyanogen and cyclohexane were prepared in the same manner and irradiated for identical time periods.

The irradiated cyclohexane was analyzed for the three major radiolysis products--hydrogen, cyclohexene, and dicyclohexyl. The radiolytic gaseous products from cyclohexane are reported to be essentially hydrogen.[14] Gas chromatographic analyses of the radiolytic gas from our irradiations showed that it was essentially hydrogen. Thereafter, hydrogen from the irradiations of pure cyclohexane was determined volumetrically. Cyclohexene and dicyclohexyl were determined by gas chromatography. The G values for these products are given in Table V.

The yield of hydrogen with increasing dose is essentially constant. Difficulties were encountered in obtaining reproducible values at the lower doses. The values however do not differ appreciably from G = 5.2 - 5.4 as found by other investigations,[15] and were adequate for determining if the hydrogen yield from irradiated cyanogen-cyclohexane mixtures differed greatly from irradiated pure cyclohexane.

The yields of cyclohexene and dicyclohexyl decreased with increasing dose. Others workers [14,15(c)] have reported a decrease in the amount of cyclohexene

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[14] H. A. Dewhurst, J. Phys. Chem., 63, 813 (1959).

[15] (a) R. H. Schuler and A. O. Allen, J. Am. Chem. Soc., 77, 507 (1955); (b) W. S. Guentner, T. J. Hardwick and R. P. Nejak, J. Chem. Phys., 30, 601 (1959); (c) G. R. Freeman, J. Chem. Phys., 33, 71 (1960).

TABLE V

G VALUES FROM CYCLOHEXANE

G Values[a]				
Hydrogen	Cyclohexene	Dicyclohexyl	Dose (ev/gm x 10^{-20})
4.8 (89)[b]	2.2 (76)	1.6 (76)	2.44
4.9 (90)	2.3 (85)	1.5_4 (85)	2.44
---	1.7 (72)	1.3_6 (72)	4.88
5.2 (77)	1.6 (77)	1.3_4 (77)	4.88
5.1 (73)	0.96 (73)	1.0_3 (73)	14.6
---	0.93 (84)	0.95 (84)	14.6

[a]The dose was determined with the ferrous ion dosimeter and electron density correction of 0.786 applied.

[b]The numbers in parentheses are the irradiation numbers.

and dicyclohexyl with increasing dose, while others[16] have reported that after an initial decrease for cyclohexene and an initial increase for dicyclohexyl, the G values were constant with increasing dose. The G values at a dose of 2.44×10^{20} ev/gm for cyclohexene and dicyclohexyl from this work are in good agreement with the reported G values[16] of 2.2 and 1.5 for cyclohexene and dicyclohexyl, respectively, after the initial decrease for cyclohexene and increase for dicyclohexyl. The values are also in fair agreement with the G_i values of 2.28 and 1.24 for cyclohexene and dicyclohexyl, respectively, reported by Freeman.[15(c)]

[16]T. D. Nevitt and L. P. Remsberg, J. Phys. Chem., 64, 969 (1960).

2. Results from Irradiated Mixtures of Cyanogen-Cyclohexane

a. Hydrogen, Cyclohexene and Dicyclohexyl. Mixtures of cyanogen-cyclohexane were irradiated for the same time intervals as pure cyclohexane. The irradiated mixture was analyzed by gas chromatography for hydrogen, remaining cyanogen, cyclohexene, dicyclohexyl, and cyclohexyl cyanide. Hydrogen cyanide was determined by difference volumetrically. Considerable difficulties were encountered in obtaining analyses for the gaseous mixture from the irradiated cyanogen-cyclohexane samples. The results obtained are listed in Table VI.

TABLE VI

G VALUES FROM CYANOGEN-CYCLOHEXANE MIXTURES

G Values			
Hydrogen	Cyclohexene	Dicyclohexyl	Dose (ev/gm x 10^{-20})
3.7 (99)[a]	0.99 (82)	0.36 (82)	2.44
2.8 (101)	1.2 (86)	0.34 (86)	2.44
3.9 (102)	---	----	2.44
----[b]	0.72 (81)	0.36 (81)	4.88
----	0.81 (88)	0.36 (88)	4.88
----	0.57 (79)	0.45 (79)	14.6
----	0.52 (80)	0.45 (80)	14.6

[a] The numbers in the parentheses are the irradiation numbers.

[b] After development of an acceptable procedure for analysis of the gaseous mixture, time did not permit obtaining any data for the increased doses.

The G values for the three radiolysis products--hydrogen, cyclohexene, and dicyclohexyl--from irradiated cyanogen-cyclohexane samples are less than the G values for these products from pure cyclohexane. Although the G values for hydrogen from the mixtures are not in good agreement, there is a decrease of about 20 to 40 per cent in the yield of hydrogen. A portion of this decrease could be attributed to the formation of hydrogen cyanide. The cyclohexene G values are about one-half of the G values for cyclohexene from pure cyclohexane for equivalent doses. Also, the G values decrease with increasing dose the same as for the pure cyclohexane. (See Table V.) The G values for dicyclohexyl from the irradiated mixtures are decreased considerably as compared with the G values for pure cyclohexane. However, the G values for dicyclohexyl from the irradiated mixtures are essentially constant with increasing dose as contrasted with the decrease in G values with increasing dose for pure cyclohexane.

b. Hydrogen Cyanide and Cyanogen. Hydrogen cyanide in the radiolytic gases from the irradiated mixtures was shown to be present by gas chromatographic analyses with both a comparison of retention times and enrichment techniques. Hydrogen cyanide was determined volumetrically by difference as the gaseous mixture consisted of hydrogen, hydrogen cyanide, remaining cyanogen, and cyclohexane vapor. Hydrogen, remaining cyanogen, and cyclohexane vapor were determined by gas chromatographic analyses. Cyanogen was present in both the gas phase and liquid phase, and the amount in each was determined with the gas chromatograph. The remaining cyanogen and the G values for hydrogen cyanide from some of the irradiations are listed in Table VII.

The G values for hydrogen cyanide, even though they are not in good agreement, indicate that hydrogen cyanide was formed in the irradiated mixtures in

TABLE VII

REMAINING CYANOGEN AND G VALUES FOR HYDROGEN CYANIDE

Irradiation No.[a]	Cyanogen			Hydrogen Cyanide
	Original Sample (ml, STP)	Remaining (ml, STP)	Consumed (%)	G Value
99	90	32	64.5	2.3
101	89	27	69.7	2.5
102	90	28	69.0	1.4

[a]Dose for each irradiation--2.44×10^{20} ev/gm.

significant amounts. The amount of cyanogen consumed for the three irradiations was fairly consistent. In order to form hydrogen cyanide with a G of approximately 2.5 and cyclohexyl cyanide with a G of approximately 20 (as determined by potassium hydroxide pellet treatment in some of the irradiations), approximately 8 ml (STP) of cyanogen would be required. Of the quantity of cyanogen consumed in each of the irradiations in Table VII, approximately 85 per cent was used by some process other than the formation of hydrogen cyanide and cyclohexyl cyanide. No other organic cyanides were identified as radiolytic products. In each of the irradiated mixtures, a brownish, insoluble material was formed. No attempt was made to characterize this material. It is likely that it is a radiolytic product formed by the polymerization of cyanogen, and is similar to the black polymer formed in the presence of alpha-rays from radon.[13]

c. Cyclohexyl Cyanide.

(1) Evidence for Cyclohexyl Cyanide. The evidence for cyclohexyl cyanide as a radiolytic product was obtained from infrared spectroscopy and gas chromatography. An irradiated sample was distilled slowly at atmospheric pressure to remove most of the cyclohexane, thus concentrating the cyclohexyl cyanide. The infrared spectra of this concentrated product showed absorption at 4.4 microns which is attributed to the cyano group,[7] (—C≡N), and compared favorably with the spectra of a sample of authentic cyclohexyl cyanide.

The cyclohexyl cyanide has been identified on two different gas chromatographic columns, an Apiezon L column and an Ucon oil LB-550-X. Identification has been by comparison of retention times and by enrichment of irradiated samples with cyclohexyl cyanide.

(2) G Values for Cyclohexyl Cyanide. A great deal of difficulty was encountered in obtaining reproducible G values for cyclohexyl cyanide. A number of experiments were tried with varying results. For these reasons, the following discussion is a chronological account of the experimental work and the results obtained in the analyses for cyclohexyl cyanide.

After a satisfactory gas chromatographic analysis for cyclohexyl cyanide was worked out, reproducible G values for cyclohexyl cyanide could not be obtained. In analyzing a number of the irradiations a second time at later dates to recheck the G values for cyclohexyl cyanide, it was observed that G values had decreased with time. This led to analyzing the irradiated mixtures for cyclohexyl cyanide as soon as possible after irradiation. The results from a number of irradiations with varying doses are given in Table VIII. From these results, the G values for cyclohexyl cyanide were about 7 for doses up to

4.88×10^{20} ev/gm and then decreased to 5 or less for a dose of 14.6×10^{20} ev/gm.

TABLE VIII

G VALUES FROM CYANOGEN-CYCLOHEXANE MIXTURES

G Values Cyclohexyl Cyanide	Dose (ev/gm x 10^{-20})
6.6 (91)[a]	2.44
7.5 (86)	2.44
7.6 (93)	4.88
6.9 (88)	4.88
5.0 (94)	14.6
4.2 (95)	14.6

[a]The numbers in parentheses are the irradiation numbers.

Two of the irradiations were analyzed for cyclohexyl cyanide at varying time intervals over a period of 35 days. It was found that the amount of cyclohexyl cyanide decreased with increasing time after irradiation. The data are given in Table IX, and the decrease is shown in terms of G values.

In an attempt to separate the cyclohexyl cyanide from the material causing the decrease, a 5 ml sample of irradiation no. 93, dose 4.88×10^{20} ev/gm, was vacuum distilled at about 2 mm pressure and 50° C. A small portion of a dark brown material did not distill at these conditions. Cyclohexyl cyanide would distill at these conditions as it has a boiling point of 72° to 73° C at 16 mm

TABLE IX

DECREASE IN CYCLOHEXYL CYANIDE WITH TIME AFTER IRRADIATION

Time After Irradiation (Days)	G Vaules, Cyclohexyl Cyanide	
	Irradiation No. 86 (Dose--2.44 x 10^{20} ev/gm)	Irradiation No. 88 (Dose--4.88 x 10^{20} ev/gm)
1	7.5	6.9
3	6.8	---
10	4.5	4.2
24	2.3	2.3
29	2.1	2.0
35	1.7	1.7

pressure. The distillate, consisting mainly of the cyclohexane plus any radiolytic material distillable at these conditions, and a sample of the nondistilled irradiated liquid were analyzed for cyclohexyl cyanide at varying time intervals. The results are summarized in Table X, with the amount of cyclohexyl cyanide expressed in G values.

From these results, it was evident that the amount of cyclohexyl cyanide in the nondistilled sample decreased with time as shown for irradiations nos. 86 and 88 in Table IX. However, the decrease was not as great in no. 93 as it was in nos. 86 and 88 at the end of 35 days. Also, the amount of cyclohexyl cyanide in the distillate was only about one-third of that present in the original material, indicating that a large percentage of the cyclohexyl cyanide was either lost or did not distill. Although the cyclohexyl cyanide in the distillate did not decrease with time, the large loss on distillation precluded the use of distil-

TABLE X

G VALUES FOR CYCLOHEXYL CYANIDE FOR
NONDISTILLED AND DISTILLED SAMPLES FROM IRRADIATION NO. 93

Time After Irradiation (Days)	G Values, Cyclohexyl Cyanide	
	Nondistilled	Distilled
1	7.6	2.2
2	6.4	2.5
12	5.1	2.6
35	3.8	2.6

lation as a recovery method.

It was then decided to try treating samples of some irradiated mixtures of cyanogen-cyclohexane according to the methods given in Table XI. The qualitative results are also given.

The quantitative results of some of these treatments from three different irradiations are given in Tables XII, XIII, and XIV.

From the qualitative results of the treatments listed in Table XI, and the G values given for cyclohexyl cyanide in Tables XII, XIII, and XIV, it is evident that the treatment with base had a pronounced effect on the amount of cyclohexyl cyanide in the irradiated sample. The G values for cyclohexyl cyanide from the 5 per cent potassium hydroxide treatment for the three irradiations are in fair agreement. In each irradiation, however, the G values were not as great as those for the potassium hydroxide pellet treatment. The G values for the cyclohexyl cyanide from the potassium hydroxide pellet treatment showed an initial increase as compared with the original mixture and then increased to a

TABLE XI

TREATMENTS OF SAMPLES OF IRRADIATED MIXTURES OF CYANOGEN-CYCLOHEXANE

Method of Treatment[a]	Qualitative Results
1. Washed with an equal volume of 5 per cent potassium hydroxide solution, washed free of base, and dried with anhydrous magnesium sulfate.	Amount of cyclohexyl cyanide was greater.
2. Washed with an equal volume of 5 per cent hydrochloric acid, washed free of acid, and dried with anhydrous magnesium sulfate.	Amount of cyclohexyl cyanide was essentially zero.
3. Washed with an equal volume of 5 per cent potassium hydroxide followed by a wash with an equal volume of 5 per cent hydrochloric acid; then washed free of acid, and dried with anhydrous magnesium sulfate.	Amount of cyclohexyl cyanide was essentially the same as obtained by washing with 5 per cent potassium hydroxide alone; unaffected by 5 per cent hydrochloric acid wash.
4. Washed with an equal volume of water and dried with anhydrous magnesium sulfate.	Amount of cyclohexyl cyanide was not affected.
5. Two potassium hydroxide pellets were added to a sample.	The amount of cyclohexyl cyanide showed an immediate initial increase and then reached an essentially constant value upon standing.

[a]Two ml samples of the irradiated mixture were used in each treatment.

TABLE XII

CYCLOHEXYL CYANIDE FROM IRRADIATION NO. 99

Time After Irradiation (Days)	G Values, Cyclohexyl Cyanide[a]			
	Original Mixture	5% KOH	KOH Pellets	5% KOH and 5% HCl
1	3.9	18.3	9.1	18.4
6	3.6	16.4	19.3	15.1
22	3.0	17.0	20.4	16.0

[a]Dose--2.44 x 10^{20} ev/gm.

TABLE XIII

CYCLOHEXYL CYANIDE FROM IRRADIATION NO. 101

Time After Irradiation (Days)	G Values, Cyclohexyl Cyanide[a]		
	Original Mixture	5% KOH	KOH Pellets
1	5.4	14.0	7.0
7	6.9	15.4	19.1
22	8.1	13.3	19.3
35	6.5	17.2	20.6

[a]Dose--2.44 x 10^{20} ev/gm.

TABLE XIV

CYCLOHEXYL CYANIDE FROM IRRADIATION NO. 102

Time After Irradiation (Days)	G Values, Cyclohexyl Cyanide		
	Original Mixture	5% KOH	KOH Pellets
1	10.1	14.7	12.5
7	10.7	15.1	18.1
21	7.9	15.9	18.1
30	7.7	15.4	18.2

[a]Dose--2.44×10^{20} ev/gm.

fairly constant value. The G values for the potassium hydroxide pellet treatment for each of the irradiations are in fairly good agreement. After treatment with potassium hydroxide solution or pellets, there was no decrease in the amount of cyclohexyl cyanide with increasing time.

The results obtained by washing a sample of an irradiated mixture with 5 per cent hydrochloric acid were unexpected indicating that the cyclohexyl cyanide was present in some basic "complex" form. Two experiments were made to give some additional information on this part of the problem. A dilute solution of an authentic sample of cyclohexyl cyanide in cyclohexane was washed with 5 per cent hydrochloric acid in the same manner as a sample of an irradiated mixture. There was essentially no decrease in the amount of cyclohexyl cyanide in the solution as shown by gas chromatographic analyses before and after the hydrochloric acid treatment. Also, a sample from irradiation no. 99

was washed first with 5 per cent potassium hydroxide and then with 5 per cent hydrochloric acid. These results are given in Table XII, and the G values for this treatment are in good agreement with those for the 5 per cent potassium hydroxide treatment alone. In addition to these results, the chromatograms from samples of the original irradiated mixtures all had considerable tailing for the cyclohexyl cyanide peak. The chromatograms of the samples treated with either potassium hydroxide solution or pellets, however, gave very sharp peaks for the cyclohexyl cyanide with essentially no tailing. These peaks were also identical with those for cyclohexyl cyanide obtained from samples of a cyclohexane solution of cyclohexyl cyanide. From all of the data, some of the cyclohexyl cyanide in the irradiated mixtures was evidently combined in some "complex" form which was destroyed by basic treatment and which was basic enough to be completely extracted by the hydrochloric acid.

It was thought that some of the cyclohexyl cyanide could be reduced to the corresponding amine, cyclohexanemethylamine, which would be extracted by an acid. A sample of cyclohexanemethylamine was prepared, and from gas chromatographic analyses, there was no evidence that any cyclohexanemethylamine was present in the irradiated mixtures.

The G values for cyclohexyl cyanide obtained by analyzing the original mixtures immediately after irradiation were not consistent. For example, a G value of approximately 7 was obtained for a number of irradiations with doses up to 4.88×10^{20} ev/gm. (See Table VIII.) The G values for irradiations nos. 99, 101, and 102 varied from 3.9 to 10.1 for dose of 2.44×10^{20} ev/gm. (See Tables XII, XIII, and XIV.) The reason for this variation is not clear. Since the treatments of a sample of each of the original mixtures--irradiations nos. 99, 101, and 102--with potassium hydroxide pellets gave G values of 18-20,

varying amounts of the cyclohexyl cyanide must have been combined in the "complex" form. Also, the results on the decrease in the amount of cyclohexyl cyanide with increasing time after irradiation for a number of irradiations were not consistent. The results for irradiations nos. 86 and 88 were in good agreement, but for the other irradiations there was considerable variation in the amount of cyclohexyl cyanide present with increasing time after irradiation. (See Tables X, XII, XIII, and XIV.) The explanation for this is not evident although it is probably due to the nature of the "complex" form.

Although there are still problems associated with the cyclohexyl cyanide in an irradiated mixture, it is evident that cyclohexyl cyanide is formed with a G in the range of 18 to 20 under the conditions employed in this work.

3. Comments on Mechanism

The radiolysis of cyclohexane has been investigated repeatedly,[17] and there are still some questions as to the mechanisms involved in the radiolysis of pure cyclohexane and of dilute solutions of cyclohexane. In view of these facts and of the insufficient data from this work, it is deemed advisable to refrain from suggesting any mechanisms for the radiolysis of the cyanogen-cyclohexane system.

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[17] See references 14, 15, and 16 and other references cited in these articles.

IV. PUBLICATION

A manuscript, "Radiation-Induced Cyanogenation of Organic Liquids," has been accepted for publication by the International Journal of Applied Radiation and Isotopes. (See Appendix.)

V. SUMMARY

The first phase of the program was concerned with determining if cyanogenation did occur when mixtures of cyanogen and representative hydrocarbons were exposed to high energy radiation. Based on evidence from infrared spectra of the irradiated mixtures, it was concluded that radiation-induced cyanogenation did occur with each of the hydrocarbons tested. The hydrocarbons irradiated in admixture with cyanogen were benzene, toluene, n-heptane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2-methylpentane, 3-methylhexane, and cyclohexane.

The second phase of the program was a more detailed study of the radiation chemistry of the cyclohexane-cyanogen system. Samples of pure cyclohexane and of mixtures of cyanogen-cyclohexane were irradiated under the same conditions, and analyzed for the major radiolysis products by gas chromatography. G values for hydrogen, cyclohexene, and dicyclohexyl were determined from both cyclohexane and the mixtures, and in addition, G values were determined for hydrogen cyanide and cyclohexyl cyanide from the mixtures. For each of the major radiolysis products, the G values were less from the irradiated mixtures than from the pure cyclohexane. The G values for hydrogen from the mixtures for the samples analyzed were less than 4. The G values for cyclohexene from the mixtures were about 50 per cent of the values from pure cyclohexane for corresponding doses. Also, the G values for cyclohexene from the mixtures decreased with increasing dose. The G values for dicyclohexyl from the mixtures decreased to a value of about 0.4 for all doses, whereas the G values from pure cyclohexane decreased with increasing dose. The G values for hydrogen cyanide for the samples analyzed were about 2. The G values for cyclohexyl cyanide, obtained by analyzing the irradiated sample immediately after irradiation, varied from

3.9 to 10.1. However, G values obtained from samples of the irradiated mixtures treated with either potassium hydroxide solution or potassium hydroxide pellets immediately after irradiation were in the range of 15 to 20. This indicated that a considerable amount of the cyclohexyl cyanide was combined in some type of a "complex," which was destroyed by treatment with base. The data are insufficient at this time to warrant the postulation of any mechanisms for the radiolysis of the cyanogen-cyclohexane system. This investigation is being continued on another contract.

Respectfully submitted:

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VI. APPENDIX

Radiation-Induced Cyanogenation of Organic Liquids

(Prepublication copy: International Journal
of Applied Radiation and Isotopes)

Radiation-Induced Cyanogenation of Organic Liquids

(Received 19 September 1962)

This is a report on a study that was undertaken to investigate the feasibility of effecting with high energy radiation direct cyanogenation of hydrocarbons with cyanogen. There are very few reports of direct cyanogenation of organic compounds. Janz[1] reported on the direct thermal cyanogenation of benzene with cyanogen and that the best conditions were 740° C and 2-3 sec contact time with cyanogen in excess. McKusick, et al.,[2] reported on the cyanogenation, effected by 2-MeV electrons, of benzene, toluene and cyclohexane with hydrogen cyanide. In this investigation n-heptane, 2-methylpentane, 3-methylhexane, 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, cyclohexane, benzene, and toluene have been irradiated in admixture with cyanogen. Irradiated mixtures were examined with infrared spectroscopy for the presence of gross cyano products. With cyclohexane, the yield of cyclohexyl cyanide was determined by gas chromatographic techniques.

Experimental

Materials

The hydrocarbons used in this work were either reagent grade or Phillips pure grade and were used without further purification. Cyanogen was obtained from The Matheson Company and used without further purification.

Radiation source

The pure hydrocarbons and mixtures were irradiated in a 12 kc Cs^{137} source[3]. The ferrous-ion dosimeter was employed and dosimetry measurements made so that essentially the same geometry was obtained as in the irradiations.

Preparation of samples for irradiation

The organic liquid was degassed by repeating several times the cycle of freezing (−70° C), evacuation, and melting under vacuum. The required amount of cyanogen from the cylinder was measured in a gas burette. The irradiation tube containing the cyclohexane was cooled with liquid nitrogen and the cyanogen was transfered from the burette to the irradiation tube by a combination of distillation and displacement with mercury. The irradiation tube was then sealed under vacuum. Pure hydrocarbons were sealed under vacuum after degassing.

Analysis

The irradiated material from the mixtures was distilled slowly through a short packed column to separate the low-boiling products and most of the original hydrocarbon from the products less volatile than the original hydrocarbon. Infrared spectra for comparison purposes were obtained on the distillate and the higher boiling products from the mixtures, the irradiated hydrocarbons and the pure hydrocarbons. In the case of cyclohexane, the irradiated mixture was also analyzed quantitatively by gas chromatographic techniques for cyclohexyl cyanide.

Results

Absorption in the 4.35 to 5.00 μ region of the infrared spectra is attributed to the cyanide (−C≡N) group[4]. Absorption in this range was absent in the spectra of the pure hydrocarbons, the irradiated hydrocarbons, and the distillate of the irradiated cyanogen-hydrocarbon mixtures. The infrared spectra of the higher boiling fraction from each irradiated cyanogen-hydrocarbon mixture showed a very strong absorption band at approximately 4.4 μ. This is strong evidence that radiation-induced cyanogenation occurred with the parent hydrocarbon and/or some higher boiling radiolysis product to give cyano-radiolysis products. The absence of absorption in the same region of the spectra of the lower boiling radiolysis products of the irradiated cyanogen-hydrocarbon mixtures indicates either that no radiation-induced cyanogenation occurred to produce cyano products more volatile than the parent hydrocarbon or that the cyano products were present in such small amounts as to escape detection.

The irradiated cyclohexane mixtures were analyzed directly by gas chromatography. The presence of cyclohexyl cyanide was shown by use of retention times and enrichment techniques. The gas chromatographic unit was calibrated for thermal response to cyclohexyl cyanide with cyclohexane solutions of cyclohexyl cyanide. G-values for cyclohexyl cyanide were about 7 for doses below 5×10^{20} eV/g and then show a decrease to a G-value of about 5 for a dose of 1.5×10^{21} eV/g. Studies are continuing with specific hydrocarbons and the results will be reported in subsequent papers.

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